TO DEVELOP A CLEAN SMELTING PROCESS FOR HIGHLY ROASTED COPPER-NICKEL CALCINES AND TO IMPROVE METAL RECOVERY

PART A: THERMOGRAVIMETRIC - GAS CHROMATOGRAPHIC ANALYSIS OF SMELTING

Final Report
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EXECUTIVE SUMMARY

The new Falconbridge Smelter Environmental Improvement Project was started up in 1978. The process circuit consists of slurry-fed fluid bed roasters for partial roasting of the nickel-copper concentrate, electric furnaces for smelting the calcine, and matte converters. The roaster gases supply sulphur dioxide to an acid plant while dilute sulphur dioxide streams from the electric furnaces and converters are vented to the atmosphere. The plant was originally designed for removal of 50% of the sulphur in the roasters; this has been increased to 55-60%. Increasing the degree of roast further would give an additional decrease in sulphur dioxide emissions by increasing the fraction converted to sulphuric acid.

When the degree of roast is increased, more heavily oxidized calcines and higher matte grades in the electric smelting furnace result and both are detrimental to smelter metal recoveries. The counter-measure is to smelt under more intensive reducing conditions by raising the reductant feedrate. Therefore, a clear understanding of the processes taking place in the charge to the electric furnace and the behaviour of coke in the reduction process is required in order to develop the proposed higher roast regime.

A thermogravimetric (TG) analyzer - gas chromatograph (GC) combination was used to examine the behaviour of electric furnace feed mixtures of calcine and coke. Because the smelting reactions involved gases to a large extent, the TG-GC combination was required for this investigation. The sample heating rate was selected to reflect the residence time in the smelting furnace. As the temperature increased, specific reactions that occurred were identified according to temperature of occurrence, quantity reacted, the rate of reaction, and the composition of the gaseous products. Additional samples were examined by arresting the process at various temperatures. The condensed phase composition was determined by chemical analysis and sections were examined metallographically and with electron-probe micro-analysis.

The behaviour of calcines roasted from 50 to 75% sulphur elimination were quantified under nitrogen and air. The effect of different levels of coke and lime additions on the smelting process were examined.

The data from this testwork, in conjunction with thermodynamic analysis, have been applied to determine the sequence of chemical reactions encountered in a unit of charge during its progress from the freeboard to the liquid slag. These are classified according to the temperature range of occurrence in Figure 8 (nitrogen atmosphere) and Figure 9 (air atmosphere). These figures constitute a graphic display of reactions within a vertical section of the charge layer in an electric smelting furnace. Heating by slag resistance in an electric smelting furnace establishes a temperature gradient, from approximately 500°C at the freeboard to 1230°C at the slag. The low temperature reactions occur partly in contact with ingress air to the furnace and Figure 9 is representative. The high temperature reactions occur at greater depth within the bed where the oxygen supply is limited both by the need for diffusion into the charge layer

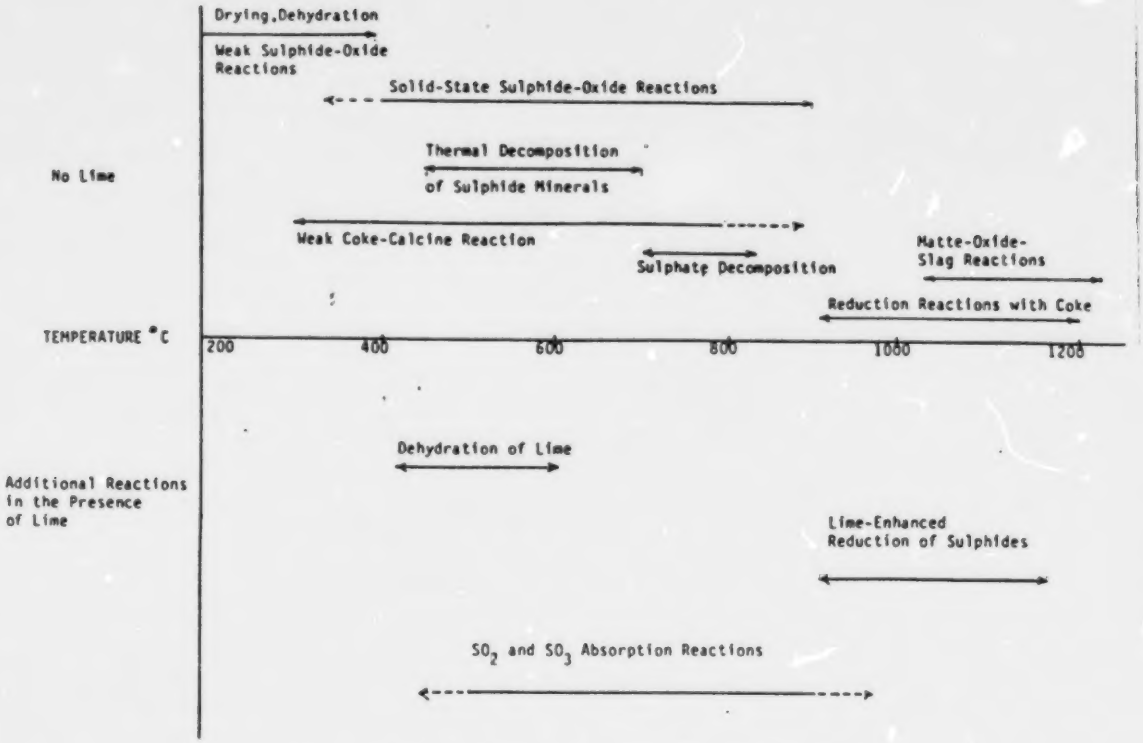

Fig. 8 Temperature Ranges for Reactions : Nitrogen Atmosphere

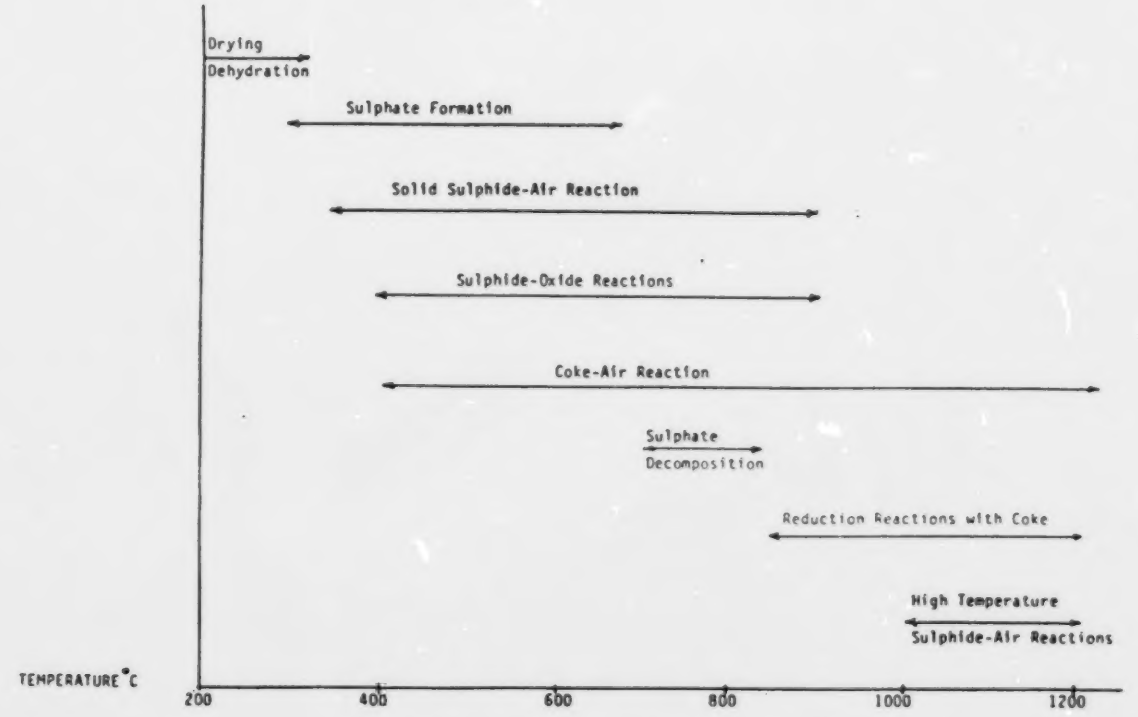

Fig. 9 Temperature Ranges for Reactions : Air Atmosphere

and the increasing reactivity of coke at higher temperatures. These reactions are represented in Figure 8.

Additional important aspects to smelting were determined and summarized in the following text.

A higher degree of roast at higher temperatures (a) produces a more inert, lower sulphide-bearing calcine and (b) improves mineral decomposition to reduce the labile sulphur level. Therefore, an inverse relationship was observed between the volume of sulphur dioxide generated during smelting and the degree of sulphur elimination from calcine by prior roasting. Thus, sulphur emissions from the electric furnace are expected to decrease at higher degrees of roast.

Original sulphates in the calcine contributed directly to sulphur trioxide and sulphur dioxide formation during smelting by undergoing thermal decomposition. Therefore, control of sulphate formation during roasting is essential.

The air-sulphide reaction depends upon the diffusion of air into the charge. Thus, sulphur dioxide formation would be depressed by operating with a deeper calcine layer in the smelting furnace.

The mass of matte formed decreases as the degree of roast is raised because of the limited quantity of sulphur and the preferential distribution of oxidized iron to the slag. Thus, a smaller quantity of higher grade matte forms when highly roasted calcines are smelted. Concurrently, valuable metals (Co, Ni, Cu) are also partly oxidized to slag to necessitate the addition of more reductant.

Coke utilization in electric smelting is primarily in the matte-assisted reduction of oxides. These reactions are very rapid and are tolerant of different coke feeds. Reductant consumption within this regime is complete and rapid and progresses readily beyond the alloy precipitation boundary.

Substantial coke burnoff occurs through contact with ingress air at temperatures above 300°C. Direct coke combustion is disadvantageous because of diminished availability for metal oxide reduction and the creation of unacceptably high freeboard temperatures in the smelting furnace. Also, some unnecessary reduction of sulphates can occur.

The primary benefit of lime addition is the absorption of SO_2 evolved in the charge heating temperature range, up to 950°C. At higher temperatures, the reduction reactions may be enhanced by lime. At high degrees of roast of calcine such as 67%, the SO_2 capture is nearly complete at lime dosages from 5% to 15%. The stable sulphur-bearing compound under reducing conditions is CaS, though $CaSO_4$ may also exist.

RÉSUMÉ

C'est en 1978 que l'on a formulé le dernier Projet d'amélioration de l'environnement pour l'installation métallurgique de Falconbridge. Il s'agit d'une part de fours à lit fluidisé alimentés de boue, servant au grillage partiel des concentrés de nickel et de cuivre, et, d'autre part, de fours électriques effectuant la fusion des concentrés calcinés, ainsi que de convertisseurs de la matte qui en résulte. Les gaz émis au cours du premier grillage alimentent une usine de fabrication d'acide, tandis que le bioxyde de soufre ayant son origine dans les fours électriques et les convertisseurs s'échappe dans l'atmosphère ambiante. A l'origine, l'installation prévoyait l'élimination de 50% du soufre au niveau du premier grillage; ce chiffre a été amené depuis à 55-60%. Une deuxième augmentation de l'intensité de grillage réduirait davantage les émissions de bioxyde de soufre avec l'augmentation de la proportion convertie en acide sulfurique.

D'une intensification du grillage il résulte des concentrés calcinés plus oxydés et des mattes d'une teneur plus élevée en métal, ce qui, dans les deux cas, agit de façon défavorable sur le taux de récupération des métaux au cours du traitement. Afin de compenser ces désavantages, il serait souhaitable d'introduire des conditions plus intensives de réduction en augmentant la vitesse d'alimentation de l'agent réducteur. C'est pourquoi une compréhension de l'action qui se poursuit dans la charge du four électrique ainsi que du comportement du coke en ce qui concerne le processus de réduction est importante si l'on veut réaliser le régime de grillage plus intensif envisagé.

A cause de la prépondérance du rôle des gaz dans les réactions chimiques ayant lieu au cours de la fusion, il a fallu, pour les besoins de notre étude, avoir recours à une combinaison de thermogravimétrie et de chromatographie pour examiner le comportement des mélanges de concentrés calcinés et de coke destinés au four électrique. La vitesse de chauffage de l'échantillon a été choisi en fonction de la durée du traitement métallurgique. A mesure que la température a augmenté, les réactions ayant lieu ont été précisées selon la température à laquelle elles se produisaient, la quantité participant à la réaction, la vitesse de réaction et la composition des gaz en résultaient. D'autres échantillons ont été examinés en arrêtant le traitement à des températures données. La composition de la phase condensée a été déterminée au moyen d'analyses chimiques et diverses sections ont fait l'objet d'un examen métallographique et d'une analyse avec microsonde électronique.

Le comportement des concentrés calcinés ayant perdu au cours du grillage de 50 à 75% de leur contenu en soufre a été quantifié en présence d'azote et d'air respectivement. On a aussi examiné les effets sur le processus métallurgique en variant les additions de coke et de chaux.

Nous avons utilisé les données obtenues ainsi que le résultat de l'analyse thermodynamique afin de déterminer l'ordre des réactions chimiques qui se produisent au sein d'une charge donnée au cours de sa progression du franc-bord jusqu'à la scorie liquide. Nous classons ces réactions selon la gamme de températures où elles se produisent (figure 8, en présence d'azote; figure 9, atmosphère d'air). Les schémas représentent les réactions ayant lieu dans une section verticale de la couche de matières à fondre à l'intérieur d'un four électrique. Le chauffage obtenu en utilisant la résistance de la scorie d'un four électrique métallurgique établit un gradient de température allant de 500°C approximativement (au franc-bord) jusqu'à 1230°C (dans la scorie). Les réactions à basse température se réalisent partiellement au contact de l'air arrivant au four, la figure 9 étant typique. Les réactions à haute température se produisent en profondeur dans le lit du four où la quantité d'oxygène est restreinte à cause, d'une part, de la diffusion obligatoire de celui-ci dans la couche de la charge, et, d'autre part, de la plus grande réactivité du coke à des températures supérieures. (Voir Figure 8).

D'autres constatations importantes relatives à la fusion ont été faites; on les examinera dans les pages qui suivent.

Un grillage plus intensif à des températures plus élevées (a) produit une substance plus inerte et contenant moins de sulfure et (b) réduit le niveau de soufre labile en favorisant la décomposition minérale. Nous avons donc constaté l'existence d'un rapport inverse entre le volume de bioxyde de soufre produit au cours du traitement par fusion et le niveau d'élimination du soufre obtenu par le grillage antérieur. Par conséquent, il est prévisible que les émissions de soufre du four électrique vont baisser avec des intensités supérieures de grillage.

Les sulfates qui se trouvent à l'origine dans les concentrés calcinés au cours du grillage se sont décomposés dans les conditions thermiques de la fusion, contribuant ainsi directement à la formation, à ce stade du traitement, de trioxyde sulfurique et de bioxyde de soufre. Par conséquent, il est essentiel de surveiller de près la formation des sulfates au stade du grillage.

La réaction air-sulfure dépend de la diffusion d'air dans la charge. La formation de bioxyde de soufre se verrait donc réduite si l'on

opérait dans une couche plus profonde de la charge.

La masse de matte produite diminue à mesure que l'on intensifie le grillage en raison du manque de soufre qui résulte et parce que la distribution du fer vers la scorie est favorisée. Donc, une quantité moindre de matte plus pure résulte de la fusion des calcinés ayant subi un grillage plus intense. Des métaux de valeur (Co, Ni, Cu) sont aussi partiellement oxydés pour former de la scorie, ce qui nécessite un dosage supplémentaire d'agent réducteur.

Dans le traitement des minerais au moyen du four électrique, le coke sert à la réduction des oxydes. Ces reactions se déroulent très rapidement et tolèrent diverses vitesses d'alimentation en coke. La consommation de l'agent réacteur suivant ce régime est complète et rapide, dépassant facilement le seuil de la précipitation des alliages.

A des températures supérieures à 300°C, il se produit la combustion de quantités considérables de coke au contact de l'air entrant dans le four. Cette combustion directe du coke a plusieurs inconvénients. D'abord, il en reste moins pour effectuer la réduction des oxydes des métaux; ensuite, il se crée des températures inacceptables au franc-bord; et, enfin, il peut en résulter une certaine réduction inutile des sulfates.

L'avantage principal des additions de chaux est l'absorption du SO_2 qui se manifeste aux températures atteintes par la charge, c'est à dire jusqu'à 950°C. A des températures plus élevées, les réactions réductrices peuvent être favorisées par la chaux. Avec des calcinés ayant subi un grillage suffisamment intense pour atteindre disons 67%, la capture de SO_2 est presque complète avec des doses de chaux de 5% à 15%. Le composé stable porteur de soufre dans les conditions de réduction est le CaS, bien que le $CaSO_4$ puisse également exister.

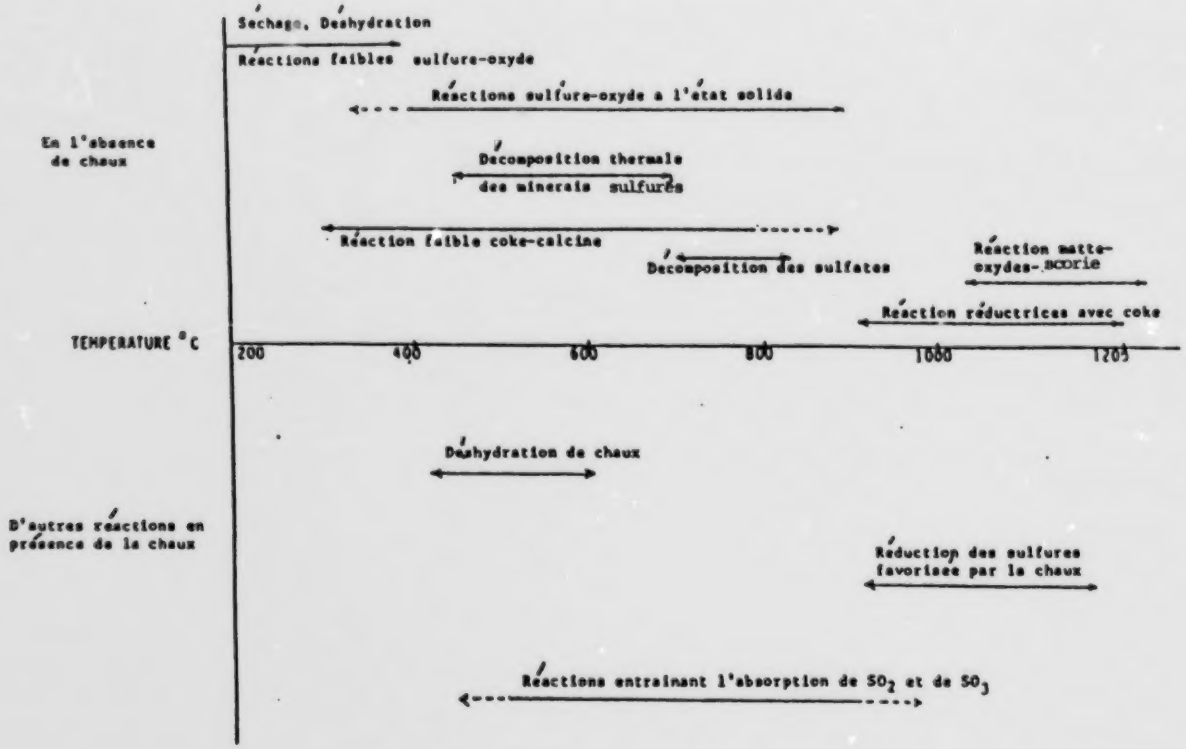

Fig. 8 Gamme de températures pour réaction: atmosphère d'azote

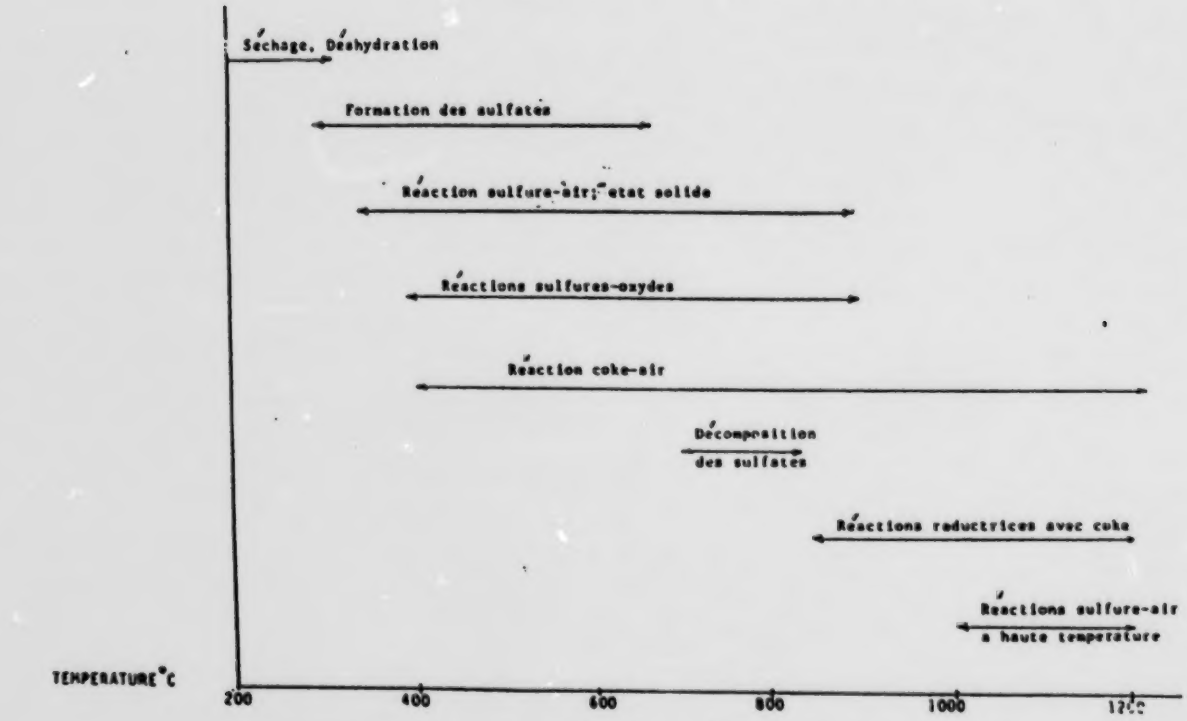

Fig. 9 Gamme de températures pour réactions: atmosphère d'air

ABSTRACT

A laboratory study was conducted to define the physical chemistry of reactions involved in the environmentally clean electric smelting of highly roasted copper-nickel concentrates.

Smelting behaviour was studied by a thermogravimetric-gas chromatographic technique in conjunction with chemical and micrographic analysis. The sequence and nature of reactions during the heating of calcines from 25 to 1250°C were identified by the temperature range and magnitude of weight changes and the characteristics of SO_2, CO, and CO_2 gas evolution. Four major variables examined were:

1) Gas atmosphere (nitrogen and air);

2) Degree of sulphur elimination from calcine (50-75%);

3) Coke addition (0-5%);

4) Lime addition (0-15%).

In the lower temperature range, (<900°C), substantial SO_2 evolution occurred from sulphide decomposition and oxidation reactions, and CO_2 from coke combustion in air. Above the fusion temperature, the dominant reaction was oxide reduction by coke in the presence of liquid matte, which acted as an oxygen transport medium.

Coke addition increases the extent and rate of reduction above 900°C, especially at levels above 3% of charge weight. Reduction is controlled by coke availability at dosages up to 5%.

Lime acts as an absorption medium for SO_2 and may participate in reduction reactions.

The significance of the experimental results is discussed in the context of electric smelting at high metal recoveries. Consideration is given to coke utilization, SO_2 release, and the implications of increasing the degree of roast of concentrate.

1.0 INTRODUCTION

A research program was undertaken to develop a clean smelting process for copper-nickel concentrate roasted to a high degree of sulphur elimination, with improved recovery of nickel and cobalt. Laboratory investigations were directed toward the definition of the metallurgical factors which are important in controlling metals recovery during reductive smelting. Part A of the study, entitled "Thermogravimetric-Gas Chromatographic Analysis of Smelting" is the subject of this report.

1.1 Background to Electric Furnace Smelting

The Falconbridge smelting process consists of fluid bed roasting of concentrates for partial sulphur elimination, electric smelting of calcine with coke, and Peirce Smith converting of matte. In the electric furnace, the smelting of calcine occurs in several stages which are delineated by the nature of the reactions involved and the temperature range of occurrence.

(a) Heating of the Charge (up to approx. 950°C)

During this period, freshly charged calcine and coke slowly proceed down into the furnace towards the liquid zone, rising in temperature from approximately 500°C at the calcine-freeboard surface to approximately 950°C at the fusion zone. As this material is heated, the reactions which occur are calcine sulphation, coke combustion, and roasting of sulphide minerals with freeboard air, as well as sulphide-oxide solid state reactions and sulphate decomposition. The oxygen balance of the furnace is affected by the sulphate formation-decomposition cycle and the consumption of some of the coke by reaction with ingress air. The quantity of oxygen presented to this stage is a function of the degree of roast of calcine. In addition, sulphur is lost from the charge as sulphur oxide gases are formed by several of the reactions.

(b) Coke Reduction and Sulphide Fusion (approx. 950 to 1150°C)

Within this temperature interval, matte formation occurs by fusion of sulphides in the calcine. The coke remaining after the charge heating period rapidly reduces iron oxides with the aid of the newly formed liquid matte, which acts as an oxygen transfer medium. The effectiveness of this mechanism influences the nickel and cobalt contents of the slag. The quantity and quality of coke added to the furnace charge affect the rate and extent of this reaction.

(c) Matte-slag Separation by Settling (approx. 1150 to 1250°C)

Within this temperature range, slag is formed by the reaction of silica flux and magnetite remaining in the calcine with iron and oxygen in matte. Matte-slag separation occurs and the matte droplets begin to settle down through the slag layer. Good phase separation is promoted by the formation of a low viscosity slag at relatively high Fe/SiO_2 ratios . However silica additions must be maintained in excess to flux the iron-rich recycled converter slag. Also, over-reduction of the calcine is necessary to produce metallized matte in the upper smelting region to reduce recycled converter slag. Therefore, the Fe/SiO_2 ratio of the slag which forms directly from the feed calcine is lowered further as iron oxide is reduced by coke in the fusion zone. The overall result is a fusion zone smelting system which consists of highly metallized matte and viscous, low Fe/SiO_2 ratio slag.

(d) Converter Slag Reduction (approx. 1200°C)

The converter slag returning to the electric furnace contains approximately 16% magnetite, and contributes a significant input of oxygen to smelting. It is believed that this slag preferentially flows to the matte-slag interface. Magnetite reduction must occur within this layer by reaction with the falling metallized matte droplets and with the bulk matte below.

The composition and quantity of the matte droplets is determined by the oxygen balance in the upper smelting regions.

(e) Matte Accumulation in the Hearth (approx. 1100°C)

Matte droplets, initially formed in the calcine layer, coalesce and accumulate in the furnace hearth after reacting with the original slag and the converter slag layer.

1.2 Laboratory Study

The investigations comprise of an examination of the initial stages of smelting, starting with the heating of the charge, then reduction by coke, fusion of sulphides, and slag formation. The purpose was to provide a sound understanding of the chemical processes which occur during the smelting of copper-nickel concentrate in the Falconbridge electric furnace, and to derive some insight into the mechanisms which may control or constrain the process result.

The study was designed to quantify the description of the important first steps in smelting in terms of the sequence of reactions, the temperature range, and the gases evolved.

Key variables were designated for this part of the research, as follows:

(a) Degree of Sulphur Elimination from Calcine during Roasting, Prior to Smelting

The current value at Falconbridge is 60%, but an increase to levels as high as 75% would ameliorate the control of sulphur distribution at the smelter. However, this advantage must be balanced against the possibility of increased metal loss to slag. For this work, degrees of roast from 50 to 75% were studied.

(b) Coke Addition to the Smelting Charge

Coke is presently added to the smelter feed at the rate of 4% on concentrate. The nature of the participation of coke in smelting reactions must be related to the efficiency of reduction of highly roasted calcines. Coke rates from 0 to 5% of charge were used in the experiments.

(c) Lime Addition to the Smelting Charge

Sulphur dioxide evolved from the calcine during electric furnace smelting is not captured. Lime was considered as a potential in situ getter, and was added at rates of 0 to 15% of charge.

The analysis of the effects of changes to these variables serves to provide a basis for new approaches towards the improvement of the reduction smelting process.

2.0 EXPERIMENTAL METHOD

Since many smelting reactions involve the transfer of sulphur and oxygen through a gas atmosphere, an experimental method was developed to monitor changes in both the condensed and gas phases. The behaviour of calcine mixtures was studied during heating to 1250°C by a thermogravimetric analyzer (TGA) - gas chromatograph (GC) combination. This method provides a correlation of weight changes and gas compositions with temperature. Chemical reactions may be identified according to the temperature range of occurrence, reaction rate, and extent.

A schematic diagram of the apparatus is shown in Fig. 1.

For each test a sample of calcine, weighing approximately 5 to 8.5 grams, was placed in a crucible which was suspended from an electronic microbalance. This device provided a continuous record of weight changes. The crucible was enclosed in a sealed Vycor reaction tube which was continuously flushed with nitrogen or air at 900 ml/min. to maintain a controlled atmosphere. The tube was heated in a Kanthal-wound resistance furnace operated by a programmable temperature controller. A heating rate of 5°C/minute was selected to simulate the full-scale smelting furnace.

Gases evolved from the charge were sampled periodically by a syringe, through a 1 mm diameter silica tube located adjacent to the crucible. The gases were analyzed for CO, CO_2, and SO_2 content by a Hewlett-Packard 5880A gas chromatograph equipped with a Poropak-Mole Sieve series column.

As the TGA-GC method alone does not positively identify chemical reactions, other techniques were employed to obtain more comprehensive data in specific cases. In some tests the heating was arrested at different temperatures and the samples were examined in several ways, as follows:

1. visual or optical examination of sections
2. chemical analysis of products
3. micrographic and electron microprobe analysis of polished sections

These provided chemical and mineralogical data to link the TGA-GC outputs with reaction mechanisms.

3.0 MATERIALS

Calcines were roasted in a fluidized bed roaster to four different degrees of sulphur elimination: 50%, 60%, 67%, and 75%. The chemical analyses of these calcines, as well as the nickel-copper concentrate from which they were prepared, are shown in Table I. The composition of the coke is also provided.

The 50% roasted calcine was silica-deficient, and quartz flux was added to adjust the iron:silica ratio in those charges. No flux additions were made to the other calcines.

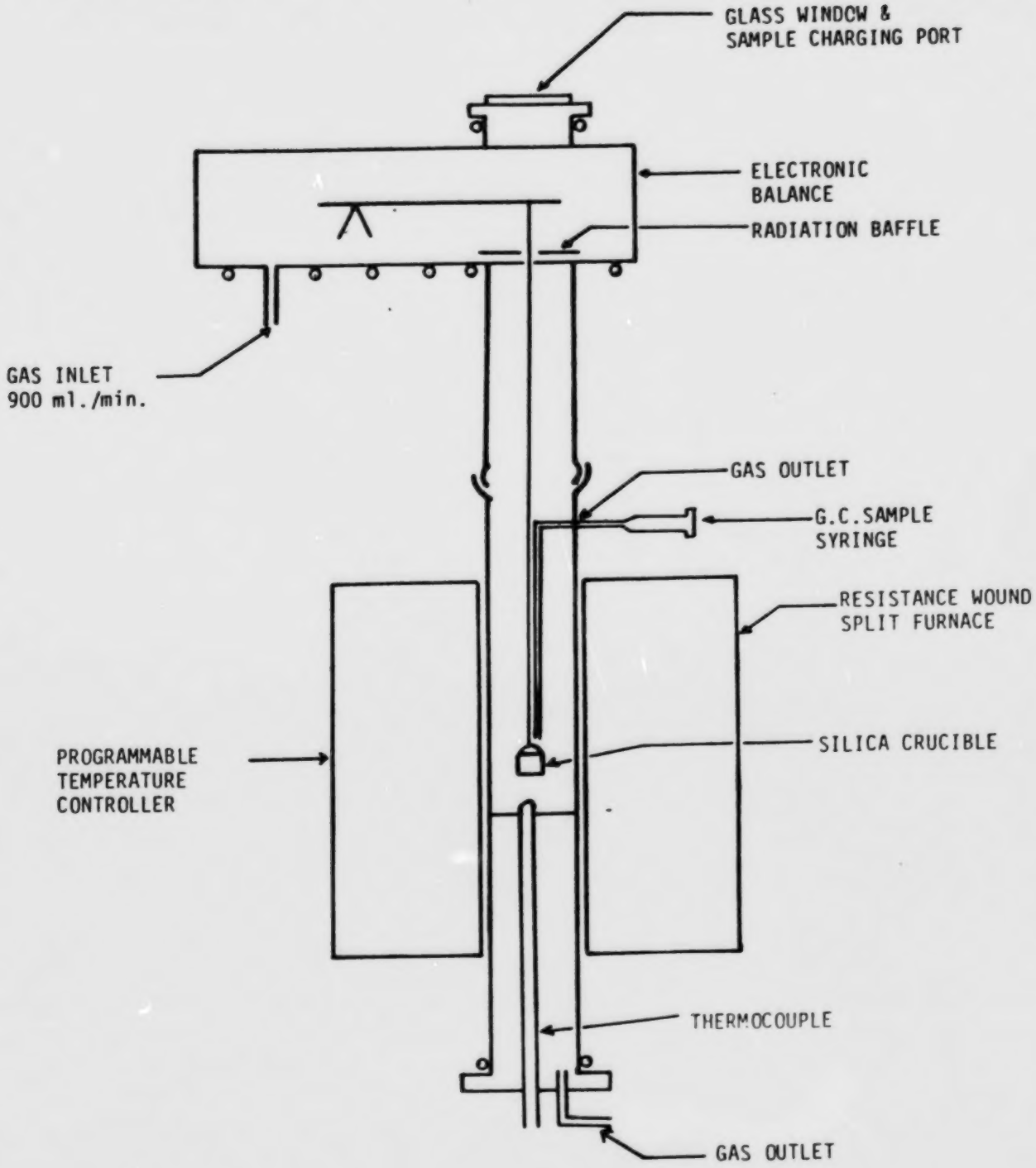

Fig. 1 Schematic Diagram of the Apparatus

TABLE 1: CHEMICAL ANALYSIS OF CALCINES AND CONCENTRATE

CALCINE

Sample No.	% Roast	Roasting Temp. (°C)	Ni	Cu	Co	Fe	S	SiO_2	SO_4	Fe_3O_4	Fe_2O_3	Al_2O_3	CaO
B4494	50	620	6.6	4.7	0.27	38	16.3	12.0	0.55	25.7	7.7	2.2	1.26
B5701	60.6	680	6.3	6.4	0.25	39	11.8	16.0	0.20	23.1	17.0		
B5705	67.5	680	5.9	6.1	0.24	36.5	9.2	19.5	0.37	15.7	21.0		
B5703	75.5	750	6.2	6.2	0.25	39	7.2	17.0	0.22	27.0	21.3		

CONCENTRATE (Typical Values %)			
Ni	6.0-6.6	Fe	41-43
Cu	4.9-6.6	S	30.2-31.6
Co	0.25	SiO_2	5.9-7.8

COKE (Imperial Oil Fluid Bed)	
Fixed C	97.2
S	3.8
Volatiles	2.4
Ash	0.38

4.0 TEST PROGRAM

Three series of tests were conducted under the conditions given in Table 2.

TABLE 2: TEST CONDITIONS

Series	Gas Atmosphere	% Coke	% Roast	% Lime
1	Nitrogen	0,1,3,5	50,60,67,75	0
2	Nitrogen	5	60,67	0,5,10,15
3	Air	0,1,3,5	50,60,67,75	0

In addition, lime only was tested in nitrogen and coke only was tested in both nitrogen and air.

The two different gas covers were applied in order to simulate the limiting conditions which exist during the smelting of a unit of charge. At the top of the charge bank, heating occurs in an oxygen-rich environment. Later, the unit of charge is substantially separated from the air, and the local atmosphere is determined by chemical reactions and rates of gas diffusion.

Separate runs were made for the arrested TGA tests, according to the schedule given in Table 3.

TABLE 3: SCHEDULE OF ARRESTED TGA TESTS

Purpose of Test	Gas Cover	% Coke	% Roast of Calcine	Temp. °C	Analysis Method
Effect of temp. on reaction mechanism	N_2	5	67	600-1250	Chemical & Micrographic
Effect of % roast on sulphate formation	Air	0	50-75	600	Chemical
Effect of % coke on sulphate formation	Air	0-5	67	600	Chemical
Effect of temp. on sulphate formation	Air	3	60	600-800	Chemical

5.0 PRESENTATION OF RESULTS

Results are reported and discussed in separate sections corresponding to the three main series of tests. Detailed results from the TGA-GC outputs are given in Appendices 1 to 3. These are in the form of graphs of weight change as a function of temperature, along with the corresponding volume % SO_2, CO, and CO_2 in the gas. To assist in discerning the effects of coke addition and degree of roast, these are plotted in two formats:

Fixed % roast; parameter = % coke

Fixed % coke; parameter = % roast

For tests carried out without carbon addition, no CO or CO_2 peaks were recorded. For certain tests which indicate a weight loss some of the gas analysis tracings are missing and were not obtained.

The large number of graphs require close inspection to yield complete information about the smelting process. For convenience, the important results within each test series are illustrated by an annotated TGA-GC graph selected from the Appendices and included within sections 6 and 8 of this report. Also given in these sections are the chemical analyses for arrested TGA tests and photographs of the crucible cross sections at the end of each run, as appropriate.

At the beginning of each section, the major phenomenological trends in weight change and gas evolution characteristics are described. Following this, the reactions which match the data are identified and the effects of the major variables are considered.

6.0 NITROGEN ATMOSPHERE, NO LIME

Complete data in graphical form are available in Appendix 1. One example of the data curves has been reproduced in the present section to form the basis for analysis and discussion of trends. This is Figure 2, "Trend Graphs for Series 1 Tests: Nitrogen Atmosphere, No Lime".

The data for a 60% roasted calcine are annotated to show qualitatively the effects of degree of roast and coke dosage on the TGA-GC response.

The graphs show that calcine charges heated under nitrogen lost weight at a moderate, nearly constant rate below 900°C, then reacted much more rapidly from 900 to 1250°C. For consideration of reaction mechanisms, these two regions are examined separately.

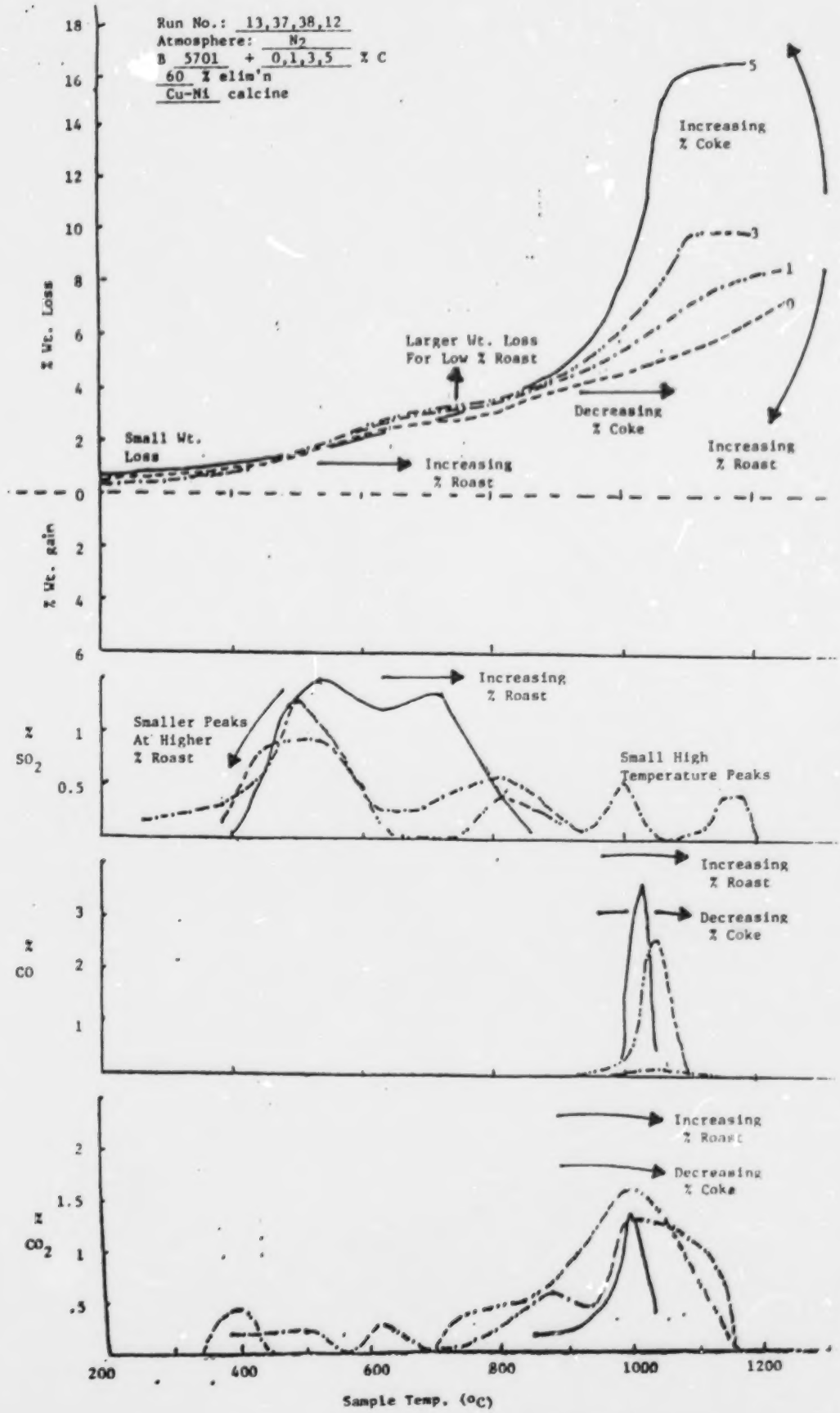

Fig. 2 Trend Graphs for Series 1 Tests:
Nitrogen Atmosphere, No Lime

6.1 Lower Temperature Region (up to 900°C)

6.1.1 Characteristic Features

(a) Weight Changes

Up to 400°C, weight losses were small (<1%), with a low rate of change. Much of the weight loss already occurred at 200°C. There is a marked increase in change at approximately 400-480°C for all samples, followed by nearly constant loss to 900°C. The loss is greater for lower % roast, but is independent of coke addition. A small inflection occurs at 650-700°C for tests at low % roast. The point of initiation of more rapid weight loss shifts to higher temperatures as the % roast increases (eg. from 420 to 470°C as % roast changes from 50 to 75%).

(b) SO_2 Evolution

Some SO_2 is produced over the entire temperature range, but major peaks appear only at 500-600°C and 800-850°C. The amount of SO_2 generated (or peak height) is lower for more highly roasted calcines, and the first peak shifts to slightly higher temperatures at higher % roast.

(c) CO/CO_2 Evolution

Low level CO_2 evolution occurs starting at 400°C, but this cannot be correlated with coke addition or degree of roast. More rapid CO_2 evolution commences near 800°C, and in some cases, a distinct peak occurs here.

6.1.2 Postulated Reactions

6.1.2.1. Low Temperature Reactions (<400°C)

The three types of reaction which occur in this region are:

- elimination of residual free moisture;
- dehydration of chemically bound water;
- weak solid state sulphide-oxide reactions or thermal decomposition of sulphides.

The occurrence of some weight loss below 200°C for most samples indicates that there is removal of small amounts of free water.

Further weight changes in the temperature range 200 to 400°C are caused by the loss of chemically combined water. As shown in Table I, the calcines contain 0.2 to 0.55% of sulphur as metal sulphates which may be hydrated. Decomposition of hydrates with water evolution typically occurs in this temperature range; eg. $CuSO_4.5H_2O$ decomposes at 250°C. The calculated weight lossses for the decomposition of pentahydrates of iron and nickel sulphates in the calcine are in the range 0.5 to 1.5%. These values correspond well with the thermogravimetric data.

The presence of some SO_2 in the offgas at temperatures below 400°C indicates that some of the reactions which are important at higher temperatures have commenced, but are weak.

6.1.2.2. Thermal Decomposition of Sulphides (450-700°C)

Bulk copper-nickel concentrate consists of sulphide minerals plus siliceous gangue. A typical mineralogical analysis of concentrate and chemical analysis of constituent sulphide minerals is given in Table 4, "Mineralogical and Chemical Data for Cu-Ni Concentrate".

TABLE 4: MINERALOGICAL AND CHEMICAL DATA FOR Cu-Ni CONCENTRATE

(A) MINERAL TYPES

Mineral	Weight Percent
Pyrrhotite	42
Chalcopyrite	15
Pentlandite	22
Gangue	Balance

(B) CHEMICAL ANALYSIS

Mineral	Wt. %					Formula
	Fe	Ni	Co	Cu	S	
Pyrrhotite	58.4	0.59	0.08	0.08	39.5	$Fe_{0.85}S$
Chalcopyrite	30.4	-	-	34.6	34.9	$CuFeS_2$
Pentlandite	29.6	36.0	1.4	0.04	33.0	$(Ni,Fe,Co)_{9.0}S_8$

During partial roasting of concentrate, some alteration of sulphides occurs. However, the flying bed roasting method employed at Falconbridge allows only a very brief residence time within the reactor, such that thermal decomposition is incomplete. Micrographic analysis of arrested TGA products heated to 600°C revealed the presence of lightly altered chalcopyrite, pyrrhotite, and pentlandite minerals. The partly roasted sulphide particles in the calcine are surrounded by iron oxides and sulphates. This indicates a largely topochemical reaction which results in the formation of a clear interface between the original reactants and the products.

Upon further heating in the temperature range 450 to 700°C, some of the residual sulphide minerals in the calcine become thermally unstable. The calculated molecular formulas for minerals in Falconbridge concentrate, given in Table 4, provide a good indication of the tendency for thermal decomposition.

For iron sulphides, the labile sulphur is readily evolved at atomic Fe/S ratios less than unity. On this basis, the behaviour of the three sulphide minerals may be described as follows:

(1) Pyrrhotite

Pyrrhotite may be considered as a sulphur-rich iron sulphide $Fe_{1-y}S$, where the value of y = 0.15 for Falconbridge concentrate. The PS_2 values given in Table 5A are applicable to the decomposition of S-rich pyrrhotite. Sulphur vapour will react with oxides to produce SO_2 as follows:

$$6Fe_2O_3 + 1/2\ S_2 = 4Fe_3O_4 + SO_2$$

Table 5A gives the equilibrium value for PS_2 during pyrrhotite decomposition along with the corresponding PSO_2 for the reaction with Fe_2O_3.

TABLE 5A: EFFECT OF STOICHIOMETRY OF PYRRHOTITE ON SO_2 EVOLUTION

T (°C)		Atomic % Fe				
		46	47	48	49	50
527	log PS_2	-3.8	-5	-7	-9.5	-14
	log PSO_2	0.56	-0.04	-1.05	-2.3	-4.5
627	log PS_2	-1.8	-3.4	-5.2	-7.8	-11.8
	log PSO_2	2.5	1.7	0.8	-1.47	-2.5

PS_2, PSO_2 are expressed in bar

(2) Chalcopyrite

The maximum thermal stability temperature of chalcopyrite is 557°C, above which complete decomposition occurs according to the following equation:

$$CuFeS_2 = iss + FeS_2$$

After the small amount of pyrite has decomposed, the PS_2 values depend upon the stoichiometry of the iss. The effect of increasing sulphur deficiency is shown in Table 5B along with the PSO_2 values arising from the reaction with Fe_2O_3.

TABLE 5B: EFFECT OF SULPHUR CONTENT OF INTERMEDIATE SOLID SOLUTION ON SO_2 EVOLUTION			
	Atomic % S in iss		
T = 627°C	48	47	46
log PS_2	-2.9	-4.6	-6.5
log PSO_2	1.98	1.13	0.18

(3) Pentlandite

Pentlandite is metal rich and relatively stable. The variable stoichiometry of natural pentlandites precludes exact thermodynamic analysis. At 600°C, the Ps_2 values over FeS-Fe and NiS-$Ni_{3-x}S$ approximate 10^{-13} and 10^{-7}atm. respectively ([5]). These are quite low compared with the values for pyrrhotite and chalcopyrite.

The thermodynamic data of Tables 5A and 5B show that significantly high PSO_2 values are available from the S_2-iron oxide reaction within a narrow temperature range. This is consistent with the observed SO_2 peaks at 450-650°C, as well as the trend towards diminishing SO_2 evolution for more highly roasted calcines.

The principal constraint on gas formation from thermal decomposition is the mass of mineral in the calcine, because the activity of sulphur drops markedly as the sulphur/metal ratio decreases. Thus, thermal decomposition is restricted, but still is sufficient to contribute to the rapid evolution of SO_2.

This mechanism is consistent with the trend towards a slower, weaker reaction as the quantity of sulphide minerals is diminished through increased degree of roast. With the greater abundance of sulphides in less roasted calcines, there is a larger weight loss and a correspondingly larger SO_2 peak. Typically, at 650-700°C, there is an inflection in the weight loss curve. This may be related to the disappearance of pyrite. At higher degrees of roast, the inflection is weak or absent. In these cases, the total weight change is quite small and the relative importance of the solid state sulphide-oxide reactions is greater; both these factors suppress the appearance of a distinct inflection.

Coke does not participate in these reactions and causes no significant differences in SO_2 evolution or weight loss behaviour.

6.1.2.3. Sulphate Decomposition (700-830°C)

The strong evolution of SO_2 at approximately 800°C is caused by the decomposition of metal sulphates in the calcine. Based upon the chemical analysis given in Table I, the calcine product from roasting contains 1 to 2.5% of metal sulphates. A micrographic analysis of a sample arrested at 900°C confirmed the disappearance of sulphates which were present at 600°C. Iron

sulphates were most evident, as may be expected from the abundance of iron in the concentrate.

The breakdown of sulphates may occur by two different mechanisms, thermal decomposition and reduction by carbon.

(1) Thermal Decomposition

The thermal stability of metal sulphates with respect to their oxides decreases as the temperature is raised. Relative stabilities of copper, nickel, and iron sulphates can be expressed in terms of their equilibrium decomposition pressures, as given in Table 6.

TABLE 6: THERMAL STABILITY OF METAL SULPHATES

Reaction	*Vapour Pressure (atm) at Temperature (°C)		
	627°C	727°C	827°C
$Fe_2(SO_4)_3/Fe_2O_3$	0.079	1.0	7.9
$CuSO_4/CuO.CuSO_4$	0.011	0.17	1.55
$NiSO_4/NiO$	1.2×10^{-3}	0.027	0.33

*Vapour Pressure = $PSO_2 + PSO_3 + PO_2$

Ferric sulphate is the least stable compound; substantial decomposition would commence at 727°C, where the vapour pressure reaches 1 atm. At temperatures above 800°C, all of these sulphates decompose by reactions of the type

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

(2) Reduction by Carbon

Metal sulphates may also be reduced by solid carbon, with the evolution of SO_2 and CO_2. Equilibrium calculations for the reactions of carbon with $CuSO_4$ and $Fe_2(SO_4)_3$ were made by use of the FACT* computer system, with the results shown in Table 7.

TABLE 7: EQUILIBRIUM PRODUCTS FOR CARBON-SULPHATE REACTIONS

Reaction	Temperature (°C)	Stable Compounds
$CuSO_4 + C$	600 and 700	$CO_2, SO_2, Cu_2S, Cu_2O,$
	750 and 800	CO_2, SO_2, Cu
$Fe_2(SO_4)_3 + C$	527 and 627	$CO_2, SO_2, Fe_2O_3, Fe_2(SO_4)_3$
	727	$CO_2, SO_2, SO_3, O_2, Fe_2O_3$

*Facility for the Analysis of Chemical Thermodynamics. Centre for Research into Computational Thermochemistry, Ecole Polytechnique de Montreal.

The thermodynamic study shows that the reduction of sulphates by carbon can occur at temperatures lower than those associated with their thermal decomposition. However, the kinetics of solid state reactions are likely to be slower than thermal decomposition reactions which require only the outward diffusion of product gases to proceed rapidly. The appearance of small CO_2 peaks in the range 600 to 800°C is associated with the reduction of either sulphates or oxides. There is evidence from the micrographic study that some sulphides were formed from the decomposition of sulphates at high coke dosages (5%).

There is little effect of the carbon addition on the TGA data near 800°C, except for the more rapid increase in weight loss at 5% coke.

The major cause of weight loss is SO_2 evolution. Carbon reduction of $CuSO_4$ produces an equal number of moles of CO_2 and SO_2, but little CO_2 was detected. Although both mechanisms of sulphate reaction are probably operative, thermal decomposition is dominant.

6.1.2.4 Solid State Sulphide - Oxide Reactions (400-900°C)

In the absence of an oxidizing atmosphere, the continuation of SO_2 evolution over a wide temperature range arises from solid state reactions of the type:

$$Me_2S + 6MeO = 4Me_2O + SO_2$$

This mechanism operates steadily, producing a background level of SO_2, rather than strong peaks at certain temperatures.

In partially roasted calcines, the concentration of both the oxide and sulphide reactants is high. Reactions with many sulphides and oxides are possible, but the high relative abundance of iron compounds in the calcine indicates that reactions which involve hematite, magnetite, and iron sulphide are most important. In Table 8, the calculated SO_2 pressures arising from several solid state reactions are shown. The PSO_2 values are sufficiently high for rapid evolution and confirm the favourable thermodynamic conditions for these reactions to proceed.

TABLE 8: THERMODYNAMIC DATA FOR SULPHIDE-OXIDE REACTIONS

	PSO_2 (atm)	
	423°C	623°C
$FeS+10Fe_2O_3 = 7Fe_3O_4+SO_2$	1.29	1.3×10^{4}
$Cu_2S+9Fe_2O_3 = Cu_2O+6Fe_3O_4+SO_2$	7.5×10^{-10}	2.9×10^{-4}
$Ni_3S_2+21Fe_2O_3 = 3NiO+14Fe_3O_4+2SO_2$	9.9×10^{-4}	107

The equations written in Table 8, represent overall reactions, and not necessarily the actual reaction path.

Rates of reaction are controlled by the availability of sulphide and oxide reactants in close proximity. During roasting, prior to smelting, the iron-nickel-copper sulphide mineral particles are partially oxidized on the outer surfaces, or topochemically. During the heating stage of smelting these particles may fracture or spall because of SO_2 evolution. Additionally, there is solid product formation at the oxide-sulphide interfaces. The SO_2 gas generated by solid state reactions must then diffuse through the calcine barrier layer to the surface. As a result of the kinetic factors, there is a sustained, moderate level of SO_2 evolution up to approximately 900°C, at which point high temperature reactions commence strongly.

6.1.2.5 Solid State Coke-Oxide Reactions (300-800°C)

Low level CO_2 evolution was noted at temperatures from 300 to 700°C, indicating the participation of coke in oxide reduction. In the absence of oxygen in the atmosphere only solid state coke-calcine reactions can occur. These are too weak to display consistent trends with coke dosage or oxide content of the calcine. Micrographic examination of arrested TGA samples confirm that coke particles are completely unaltered at 600°C, and are largely unreacted at 1000°C. At approximately 800°C stronger CO_2 evolution occurs, first through carbon reduction of metal sulphates, and then through high temperature reactions.

6.2 High Temperature Region (Above 900°c)

6.2.1 Characteristic Features

(1) Weight Changes

A very rapid increase in weight loss occurs near 950°C; it is a strong function of coke addition, but nearly independent of degree of roast. The initial temperature for this phenomenon decreases at higher coke additions, from about 900°C for samples with 5% coke to above 1000°C for those with no coke. It is also delayed at higher % roast.

(2) SO_2 Evolution

The evolution of SO_2 at temperatures between 950 and 1200°C is characteristic of samples with low coke addition (0 and 1%). Peaks are found at approximately 1000°C and 1150°C, but lower level SO_2 generation does occur throughout the temperature range. The quantity of SO_2 is greater at lower % roast, and decreases as more coke is added to the charge.

(3) CO/CO_2 Evolution

Strong CO and CO_2 evolution occurs from 900 to 1200°C for samples which contain coke. Peaks are centered around 1000-1100°C, and occur earlier for larger coke additions. Peak positions shift to higher temperatures as % roast increases. The maximum peak $CO:CO_2$ ratios are a function of coke addition, and increase markedly as the coke rate changes from 3% to 5%.

6.2.2 Postulated Reactions

6.2.2.1 Reduction Reactions

The high temperature region of the tests conducted under nitrogen corresponds most closely to the actual smelting stage in the electric furnace. During the heating of charge from about 900°C to 1250°C several important processes occur, as follows:

1. sulphide fusion to form liquid matte
2. reduction of oxides, mainly by coke via dissolution in matte
3. fusion of flux, gangue and oxides to form slag
4. separation of matte and slag phases

The compositions of matte and primary slag are determined by inputs or mass constraints and thermodynamic conditions, chiefly the oxygen potential of the system. These are substantially set by the two variables which were studied during the TGA-GC testwork:

1. degree of roast, which establishes the oxygen and sulphur input to smelting

2. coke addition, which provides a capacity for oxygen removal from the charge.

The phenomena associated with changes to these two variables are now considered.

6.2.2.2 Effect of Degree of Roast

The roasting of sulphide concentrates results in the simultaneous removal of sulphur as SO_2 and the addition of oxygen to the calcine as Fe_3O_4, Fe_2O_3, NiO and other oxides. Sulphur removal from the charge induces a change in the overall matte composition towards the metal solubility limits. This trend may be traced through Figure 3, which shows the estimated metallic saturation boundaries in the (Ni + Cu)-Fe-S system. At high degrees of roast, as employed by Falconbridge, sulphur availability is limited to the extent that metal precipitation occurs. Alloy and liquid matte compositions vary along the endpoints of the liquidus tie lines in the ternary diagram.

Increased sulphur removal through roasting causes several changes to the matte phase:

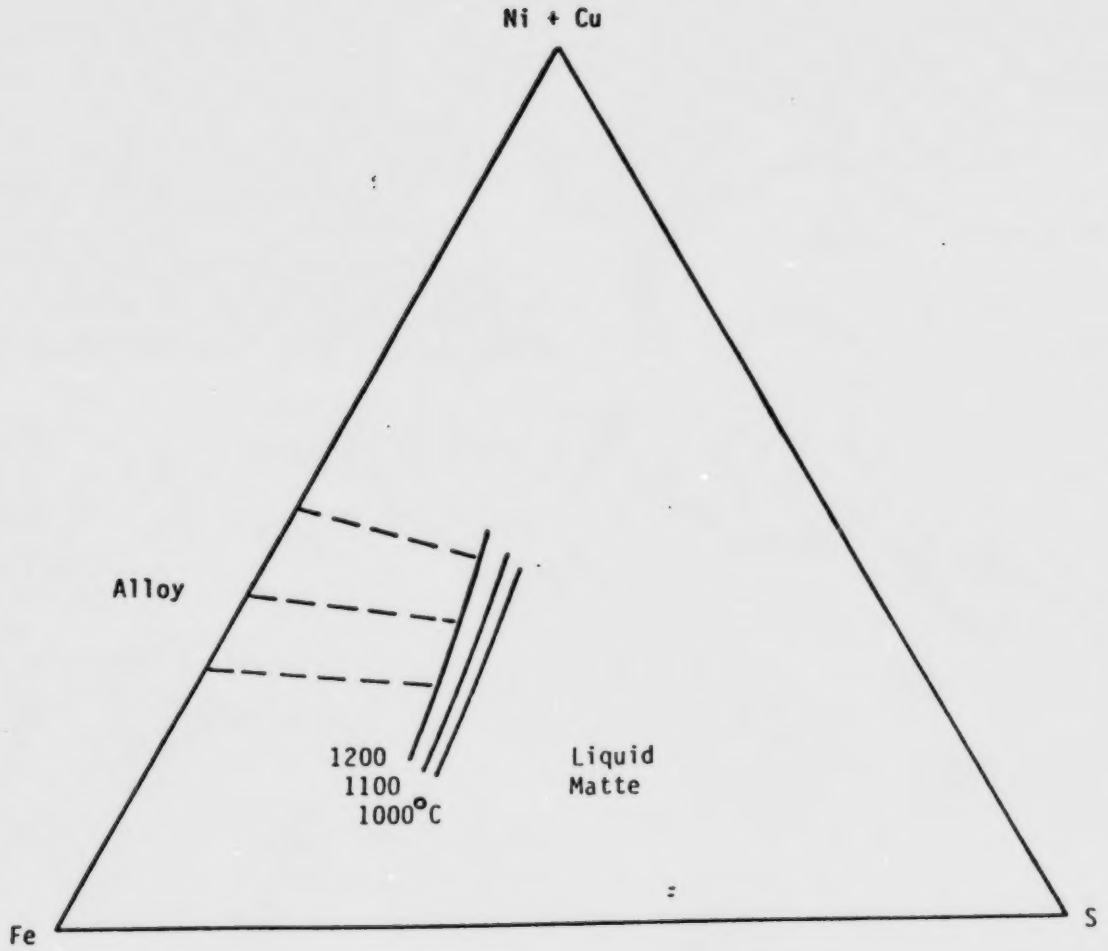

Fig. 3 Estimated Metallic Saturation Boundaries in the (Ni + Cu)-Fe-S System

1. the composition of metallics shifts towards a higher $\frac{Ni + Cu}{Fe}$ ratio
2. the mass ratio of metallics to liquid matte increases
3. the mass of matte decreases

The influence of sulphur content in calcine is evident in Figure 6, which contains photographs of sections of crucibles taken after reaction to 1250°C. As the degree of roast rises from 50 to 75%, the volume of the matte phase clearly diminishes. This trend is particularly evident at low coke dosages because the dilution of matte with iron-rich metallics from carbon reduction of oxides is relatively small.

Along with the increase in the fraction of metallics in matte at higher degrees of roast, there is a corresponding increase in the overall matte grade, %(Cu + Ni + Co). The relative enrichment of metallics in Cu + Ni + Co is consistent with a higher oxygen potential in the system. However, the higher matte grade and oxygen potential are conditions which promote greater losses of Cu, Ni, and Co to slag through increased metal solubility and primary slag burden. Since the rationale for operation with higher degrees of roast is control of sulphur distribution in the smelter, reductant addition to the electric furnace is essential.

Sulphide availability also affects the initiation temperature of the rapid weight loss period. Weight losses in the high temperature region are caused by only the following two types of reactions:

1. reduction of solid oxides by coke via FeO dissolution in matte, forming CO and CO_2
2. oxide reactions with liquid matte, with SO_2 evolution; these reactions are much weaker than carbon reduction

In both cases the quantity of residual sulphides available for matte formation influences the contact surface area between matte, oxide, and coke (if present).

6.2.2.3 Effect of Coke Addition

In the absence of carbon, little weight change occurs above 950°C at all degrees of roast. Matte fusion and slag formation proceed but reduction can only occur by the relatively weak reactions with FeS, which are discussed later.

With the addition of coke the TGA curves are affected in two ways:

1. weight loss due to oxygen removed from the charge
2. weight loss due to the loss of coke itself

Micrographic examinations show that the coke is completely consumed even at the 5% addition level. Thus, weight losses in Figure 2 are considerably magnified

by the mass of coke. If adjustment is made for this factor, then the high temperature curves are compressed closer, but with the same relative positions which correspond to the relative amounts of oxygen reduced from the charge.

The addition of coke to the charge causes a decrease in the oxygen potential of the system and provides a reductant for ferric iron. As a consequence the matte becomes more metallized by iron. On the (Ni+Cu)-Fe-S phase diagram in Figure 3, the addition of coke at any degree of roast corresponds to a shift in the overall matte composition towards the iron corner. For highly roasted calcines the matte becomes metal saturated, and a further effect is the increased mass of metallics compared with liquid matte as the reduction continues. Both matte grade and % sulphur content decrease as the dilution of matte by iron causes an increase in the total mass of matte. In Figure 6 the crucible cross-sections at the end of the tests show that there is an increase in the volume of matte (sulphide plus metallics) as the coke dosage rises from 0 to 5%. This is most evident at high degrees of roast because the quantity of metal sulphide is restricted by sulphur availability.

Another reason for the lower matte grade at high coke dosages is that there is less sulphur loss from the system when coke is available as a reductant. The reduction of oxides by FeS with SO_2 evolution is suppressed by carbon reduction. Thus, sulphur elimination during reductive smelting is lower than during "oxidizing" smelting.

The compositions of the metallics in equilibrium with liquid matte provide an index of the oxygen potential of the system at any time during smelting. In Figure 3 the alloy composition shifts towards a lower $\frac{Cu + Ni}{Fe}$ ratio with increasing coke content. Above approximately 1150°C the matte also approaches equilibrium with liquid slag, which may be considered in simplified form to be iron silicate. The region of liquid slag compositions is shown on the $FeO-Fe_2O_3-SiO_2$ ternary phase diagram in Figure 4 in the fayalite area; equilibrium oxygen pressures are also indicated. Oxygen isobars may also be identified as lines of constant alloy composition, expressed in terms of the $\frac{Cu + Ni}{Fe}$ ratio.

Under conditions of metal and silica saturation the system becomes univariant, such that the alloy composition cannot change independently of Po_2. At 1200°C this value of Po_2 varies from about 3.5×10^{-13} atm at Fe saturation to 10^{-8} atm for Ni saturation.

The progress of reduction by carbon in the temperature range 900-1200°C may be followed with reference to the chemical analyses provided in Table 9, the micrographic results from arrested TGA tests, and the experimental TGA-GC curves. These data are complete for the tests at 67% roast with 5% coke addition.

At 900°C the low temperature reactions are substantially complete and the charge consists of partly altered sulphide, oxide, and silicate constituents which form

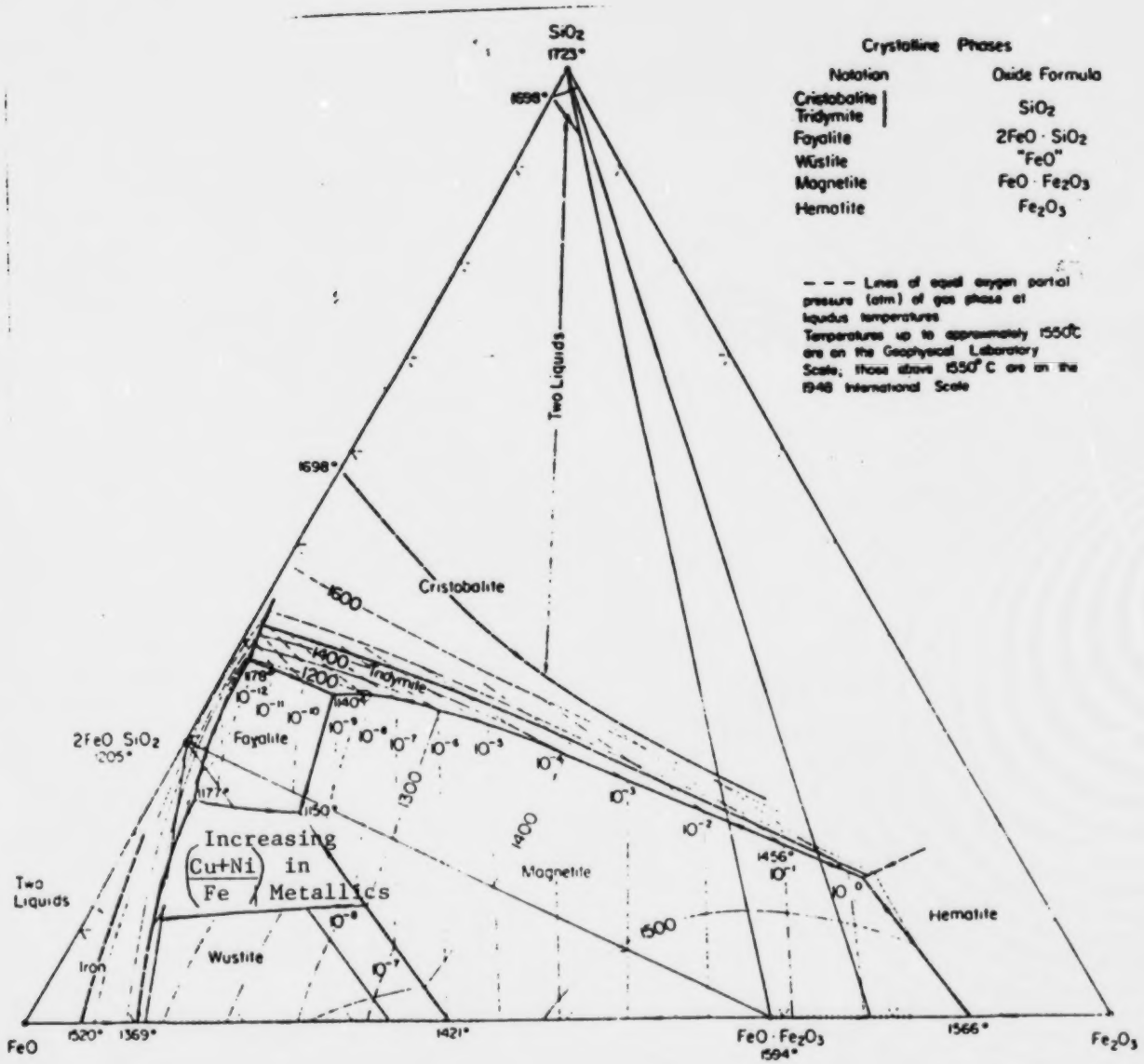

Fig. 4 The FeO-Fe_2O_3-SiO_2 System

Phase Diagram for Ceramists, E.M. Levin, C.R. Robbins, H.F. McMurdie
The American Ceramic Society, Columbus, Ohio, 1964.

a porous sinter. Incipient metallization is apparent at 960°C, giving metallic contents of 1.16% Ni, 1.58% Fe, and 0.42% Cu. There is a decrease in Fe^{3+} from 22.5% at 600°C to 17.9% at 960°C, this is an indication of some gaseous CO and direct carbon reduction. However, the strongest reactions occur just above the matte fusion temperature, at 1000-1060°C. The large weight losses as well as CO and CO_2 peak maxima in this range are consistent with the appearance of the charge which provides much evidence of reaction among matte, flux, and graphite. Metallization becomes extensive and most of the magnetite disappears.

From 1060°C to 1250°C there is diminished weight change and gas evolution, coincident with coke depletion. Complete fusion and slag formation occur while metallization progresses further. The composition of metallics also changes with temperature according to the data of Table 10.

TABLE 10: CHEMICAL COMPOSITION OF METALLICS

Temperature	Composition (wt%)				Fe/Ni wt ratio
	Fe	Cu	Co	Ni	
1056°C	62.5	4.57	1.63	32.8	1.91
1100°C	65.2	4.07	1.47	31.4	2.08
1250°C	73.4	4.14	1.21	21.9	3.35

The important trend is the increasing enrichment of the metallics with iron. There is a rise in the Fe/Ni ratio from 1.9 to 3.4 as reduction proceeds towards complete exhaustion of coke.

The influence of the quantity of coke on the high temperature reduction reactions is also displayed by the shapes of the weight loss curves, which are not very different for various degrees of roast, at a constant coke dosage. Curves are displaced by the differing weight losses in the lower temperature region, but could be superimposed to form a single characteristic reduction curve for a given coke addition. Thus, oxide reduction is controlled by coke availability in the range 0-5% coke. The concentration of oxides in calcine is sufficient for complete coke consumption in reduction reactions at the degrees of roast employed in these tests.

The effect of coke dosage on the initiation temperature for rapid reduction is evident in the weight loss curves. A greater quantity of coke presents a larger surface area for reactions with matte and also augments the probability of CO regeneration by reduction of CO_2 at the coke surface. Peak measured CO/CO_2 volume ratios are given as a function of the coke additions in Table 11.

TABLE 9: CHEMICAL ANALYSIS OF PRODUCTS FROM ARRESTED TGA TESTS

EFFECT OF TEMPERATURE (Nitrogen Atmosphere)

% Roast	% Coke	% Lime	T (°C)	Ni	Ni°	Fe	Fe°	Cu	Cu°	S	S^{04}	Fe^{3+}	Fe_3O_4
67.5	5	0	600		0.08		0.03		0.46			22.5	
			900		0.46		1.04		0.40			19.6	
			960		1.16		1.58		0.42			17.9	
			1000	6.3	2.5	38	5.2	6.3	0.56	8.2	<0.03	11.0	22.9
			1056	6.8	4.0	41	19.1	6.5	0.64	8.9		2.24	4.6
			1100	6.7	3.9	41	17.6	6.7	0.68	7.6		1.02	2.1
			1250	10.6	9.2	47	25.2	10.3	0.83	12.0		1.0	2.0

TABLE 11: PEAK CO/CO_2 RATIOS	
% Coke	Range of CO/CO_2 Ratios
1	0.3-0.6
3	0.35-1.5
5	1.5-2.6

The increasing CO/CO_2 ratios at higher coke dosages correspond to more reducing conditions in the charge, but also imply a lower efficiency of coke utilization.

6.2.2.4 Reduction Mechanisms

The reduction of a metal oxide, MeO, in the presence of solid carbon may be simply expressed by reactions MeO + C = Me + CO and MeO + CO = Me + CO_2. However, the observed rapid reaction rates in the temperature range of 950-1100°C are inconsistent with the known kinetic constraints on the reduction of oxides by CO or directly by carbon. The formation of liquid matte is critical to the establishment of rapid kinetics. Liquid matte bears the capacity to act as an oxygen transfer medium between solid oxides and coke. This matte-assisted reduction mechanism is promoted by several characteristics of liquid matte, as follows:

1. High oxygen solubility (approximately .6 wt% for a 20% Cu, 20% Ni matte).

2. Low fusion temperature. The fusion point of matte is typically <1000°C, and is significantly below the lowest melting point of slag.

3. High fluidity. Liquid mattes provide rapid, good contact between solid oxides and coke particles.

The rapid dissolution of magnetite into FeS and copper matte has been demonstrated previously in experiments reported by Kaiura([1]) and Lindon([2]). These studies showed that reduction by carbon in contact with matte was much more likely than the FeS-Fe_3O_4 reaction, with SO_2 evolution. Such behaviour is congruent with the results of the TGA-GC tests, which showed no SO_2 production in the fusion region at high coke addition levels.

Other possible reduction mechanisms are significantly less favoured than the matte-assisted reaction. Solid state carbon-oxide reactions are severely limited by contact area and would not exhibit the strong temperature dependence which was observed. Gaseous reduction by CO is thermodynamically possible at temperatures above the equilibrium value for the coexistence of MeO, Me, CO, CO_2 and solid carbon. At a total pressure, $P_{CO} + P_{CO2} = 1$ atm, the reduction of all Cu, Ni, Co, and Fe oxides of interest should proceed at temperatures above 650°C. However, the regeneration of product CO_2 at the solid carbon surface by the Boudouard reaction $C + CO_2 = 2CO$ is known to be slow below 1000°C.

The sequence of magnetite reduction by carbon through the liquid matte intermediate may be considered to be sequential, as follows:

$$Fe_3O_4\ (S) = Fe_3O_4\ (\text{dissolved in matte})$$

$$Fe_3O_4\ (\text{in matte}) + C = 3FeO\ (\text{in matte}) + CO\ (g)$$

$$FeO\ (\text{in matte}) + C = Fe\ (\text{in matte}) + CO\ (g)$$

The overall reaction then, is:

$$Fe_3O_4(s) + 4C(s) = 3Fe\ (\text{in matte}) + 4CO\ (g)$$

In terms of reduction by CO this becomes:

$$Fe_3O_4(s) + 4CO\ (g) = 3Fe\ (\text{in matte}) + 4CO_2\ (g)$$

The result of this reaction is the formation of an iron-rich, sulphur deficient matte which can reduce copper, nickel, and cobalt oxides from slag. An increase in the coke addition causes the formation of a larger mass of a lower grade matte which thereby has a greater capability for FeO dissolution.

At higher temperatures slag formation can occur either directly from fusion of flux with oxides, or through the matte by reactions such as the following:

$$2FeO\ (\text{in matte}) + SiO_2 = 2FeO.SiO_2\ (1)$$

$$3FeO.2SiO_2\ (1) + FeO\ (\text{in matte}) = 2(2FeO.SiO_2)\ (1)$$

Thus, when liquid slag has formed, oxygen removal from matte can occur via FeO solution in slag; however, the solubility of FeO in slag is fixed by the matte-slag equilibrium.

From the TGA-GC data it is clear that the rate of oxide reduction in the temperature range 950-1100°C exerts a dominant influence on the smelting rate of partly roasted calcines.

6.2.2.5 High Temperature SO_2 Producing Reactions

In the tests at 0 and 1% coke additions there is a moderate increase in the rate of weight loss above 950°C. In the presence of coke some of this weight change is caused by CO_2 evolution, but for 0% coke the observed loss can only occur by SO_2 escape. The evolution of a small quantity of SO_2 above 900°C, with peaks at approximately 1000°C and 1150°C, is caused by the reaction of liquid matte with oxides in the calcine.

Liquid matte, formed by the fusion of nickel, copper, and iron sulphides at about 950°C, can dissolve a substantial quantity of oxygen as FeO. There is an abundance of magnetite in the calcine which may be reduced by FeS in the matte as follows:

$$3Fe_3O_4\ (\text{solid}) + FeS\ (\text{in matte}) = 10FeO\ (\text{in matte}) + SO_2$$

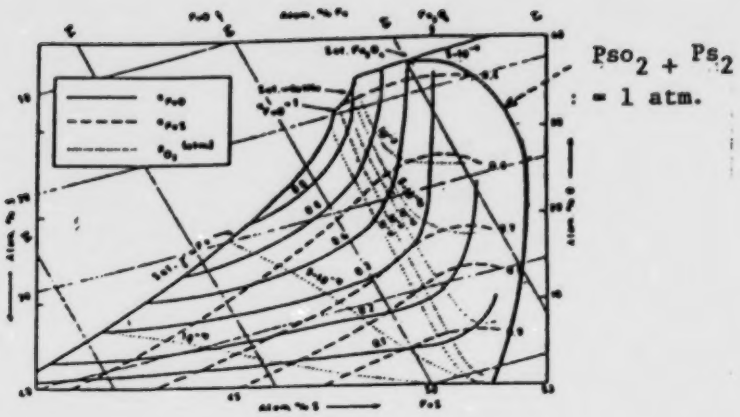

Figure 5: The Fe-S-O Activity Diagram at 1200°C

The discharge of SO_2 can only occur at high P_{SO_2}, say 0.01 atm. and above. There are insufficient thermodynamic data for the Cu-Fe-Ni-S-O system to define the required conditions, but a good indication is available from the Fe-S-O activity diagram of Stofko et al[3], shown in Figure 5.

Upon formation of liquid FeS in matte the dissolution of magnetite occurs rapidly. Near magnetite saturation a sufficiently high P_{SO_2} for evolution can be achieved. With further dissolution the liquid composition moves towards the Fe_3O_4-'FeO' saturation point where the P_{SO_2} value is less than 0.01 atm., and the formation of SO_2 gas is depressed.

The second SO_2 peak occurs in the temperature range of flux melting and slag formation. In silica saturated fayalite slags at 1200°C the activity of FeO is fixed at about 0.4. Along the magnetite saturation boundary of the Fe-S-O system the value of $P_{SO_2} + P_{S_2}$ increases rapidly as aFeO falls below unity, leading to the second burst of SO_2 at 1150°C.

The degree of roast of calcine affects the strength of high temperature SO_2 production by controlling the availability of FeS, or the matte grade. Oxygen solubility is higher in the low grade mattes formed at low % roast, thereby giving rise to larger P_{SO_2} values. Coke addition to the charge depresses SO_2 evolution by removing oxygen from the matte. With sufficient coke (3% or more) the reduction of oxides occurs through the liquid matte medium, without SO_2 generation.

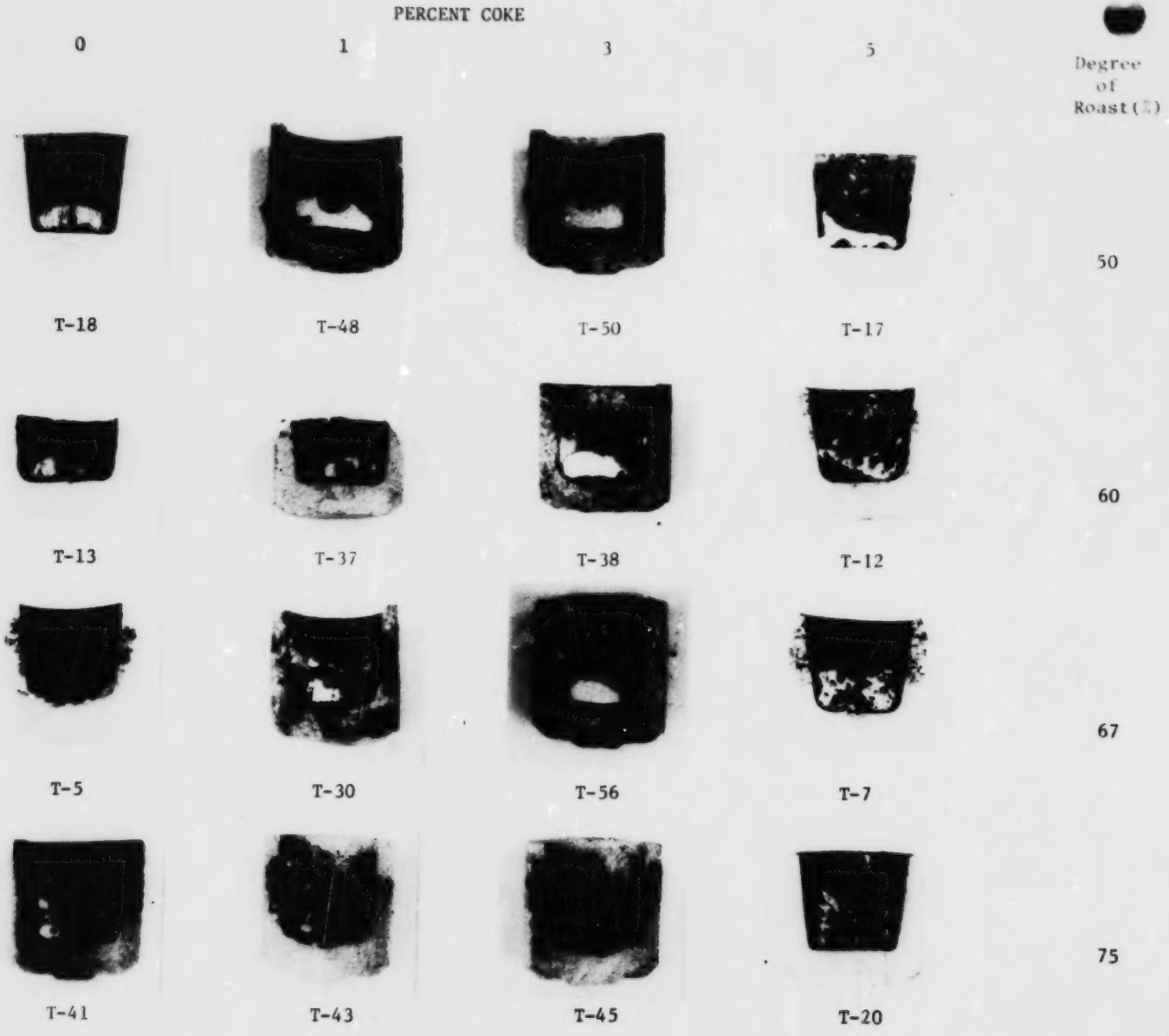

FIGURE 6: CRUCIBLE CROSS SECTIONS FOR SERIES 1 TESTS.

7.0 NITROGEN ATMOSPHERE: 0-15% LIME ADDITION

Lime was added to the calcine charges to examine the effects on SO_2 evolution and the progress of smelting reactions. Two sets of tests were performed as follows:

1) 67% roast, 5% coke; 0, 5, 10, 15% lime
2) 60% roast, 5% coke; 0, 5, 10, 15% lime

Complete graphical data for these runs as well as lime alone are presented in Appendix 2.

7.1 Lime Alone: Modification of TGA Curves to Correct for Moisture in Lime

The TGA curve for lime heated in a nitrogen atmosphere displays a 24% weight loss in the temperature range 420-600°C, with little CO_2 evolution; this is caused by water loss. Complete dehydration of $Ca(OH)_2$ according to reaction $Ca(OH)_2 = CaO + H_2O$ involves a weight loss of 24%, with P_{H2O} values of 0.15 atm at 427°C and 1.32 atm at 527°C.

At the higher lime addition levels used in these tests (10 and 15%) the weight loss curves are considerably affected by the discharge of water vapour. Since the dehydration reaction has no functional involvement in the smelting process, adjustments have been applied to the curves, and these graphs are also included in Appendix 2. The analysis of data refers to the adjusted values.

7.2 Calcine - Lime Mixtures

7.2.1 Characteristic Features

(1) Weight Changes

The adjusted weight change curves for tests which contain 5, 10, and 15% lime are very close at each degree of roast. There is less weight loss for these mixtures throughout the temperature range than for lime-free charges. With no lime there is a steady, moderate weight loss from 600°C onwards, until rapid reaction occurs at 950-1000°C. By comparison, the charges with added lime have small weight losses up to 800°C (<1%), then a rapid increase at a lower temperature, approximately 900°C.

(2) SO_2 Evolution

Very little SO_2 evolution is observed in the presence of lime, but baseline values for 0% CaO are lacking. Comparisons with the corresponding tests in Series 1 at 3% coke dosage show that lime addition greatly depresses SO_2 evolution.

(3) CO/CO_2 Evolution

In all cases the evolution of CO and CO_2 occurs strongly only above 850°C. The most notable effects of lime addition are:

- large increase in peak heights
- broader peaks, indicating discharge over a wider temperature span
- evolution commences strongly at lower temperatures (850°C instead of 950°C).

7.2.2 Postulated Reactions

Those chemical reactions which occur in lime-free tests carry on, but are joined by reactions which involve lime. The influence of lime addition is considered for lower temperature reactions, from which SO_2 is usually produced, and for higher temperature reduction reactions.

7.2.2.1 SO_2 and SO_3 Absorption Reactions

The general absence of SO_2 in the outlet stream shows that the gases produced by the thermal decomposition of sulphides and sulphates, as well as sulphide-oxide solid state reactions, are absorbed by lime. Two products are possible for these absorption reactions, $CaSO_4$ and CaS. The stabilities of these two are influenced by temperature, supply of carbon, and oxygen potential. Under the test conditions of Series 2 there is no atmospheric oxygen available for the formation of $CaSO_4$, so CaS is more likely to form.

In the temperature range 450-700°C, SO_2 is produced from the thermal decomposition of sulphide minerals. An equilibrium analysis of the reactions which occur when pyrite in the charge is heated with lime and carbon is shown in Table 12.

TABLE 12: EQUILIBRIUM PRODUCTS FOR REACTION $FeS_2 + Fe_2O_3 + CaO + XC =$

Temperature (°C)	X (= Moles Carbon)	Major Stable Products
600	0	0.33 $CaSO_4$, 0.67 CaS, FeS, Fe_3O_4
600	0.1	0.28 $CaSO_4$, 0.72 CaS, FeS, Fe_3O_4, CO_2
600	1.0	1.0 CaS, FeS, Fe_3O_4, CO_2, CO, C

In the absence of carbon the formation of $CaSO_4$ is favoured, but limited by the supply of oxygen for the reaction $CaO + SO_2 + 1/2\ O_2 = CaSO_4$. This results in the formation of both $CaSO_4$ and CaS. With carbon added to the charge $CaSO_4$ is reduced to form CaS plus CO and CO_2. The greater concentrations of these gases detected in the range 600-800°C at 5-15% CaO arise from this reduction.

As long as sufficient carbon is present to maintain strongly reducing conditions, any $CaSO_4$ will react to form CaS throughout the charge heating temperature range. There is little temperature effect on the equilibrium compositions shown in Table 12 from 500°C upwards.

At approximately 750-800°C metal sulphates in the calcine become thermally unstable with respect to oxides, producing SO_3 partial pressures greater than 1 atm. Under these more oxidizing conditions lime reacts to form calcium sulphate:

$$CaO + SO_3 = CaSO_4$$

The thermodynamics of this reaction are highly favourable, as the equilibrium P_{SO3} at 800°C is 10^{-10} atm. With carbon in the charge, reduction of both metal sulphates and $CaSO_4$ can occur, again to produce CaS. The equilibrium products of iron sulphate decomposition in presence of coke and lime are presented in Table 13.

TABLE 13: EQUILIBRIUM PRODUCTS FOR REACTION $yFe_2(SO_4)_3 + C + CaO$ =

Temperature (°C)	Y(=Moles Ferric Sulphate)	Major Stable Products
800	1	$CaSO_4$, Fe_2O_3, SO_2, CO_2
800	0.1	CaS, CaO, Fe, FeO, CO_2,CO

The results in Table 13 show that the products of sulphate decomposition and reduction are altered according to the relative amounts of metal sulphate, lime, and carbon. In test series 2, there is a large excess of CaO and the coke in the charge has not been consumed prior to the high temperature reduction phase; thus conditions at y=0.1 are more applicable. There is complete absorption of SO_3 from ferric sulphate, resulting in the formation of CaS and evolution of CO and CO_2. The sharp rise in the CO_2 peaks at 800°C for lime-containing charges is consistent with the position of sulphate decomposition reactions.

7.2.2.2 Reduction Reactions

The major feature of tests with added lime is the large increase in CO and CO_2 volumes in the reduction temperature region. This phenomenon could be caused by the lime-enhanced reduction of sulphides by either of two reactions:

$$MeS + CaO + 1/2C = Me + CaS + 1/2\ CO_2 \quad \ldots\ldots\ldots \quad (1)$$

$$MeS + CO + CaO = Me + CaS + CO_2 \quad \ldots\ldots\ldots \quad (2)$$

At 927°C both of these reactions are thermodynamically favoured. This is evident from the large values of the equilibrium constants for the sulphides of interest in Table 14.

TABLE 14: EQUILIBRIUM CONSTANTS FOR LIME-ENHANCED REDUCTION OF SULPHIDE		
Sulphide	Equilibrium Constant at 927°C K(1)	K(2)
Ni_3S_2	57.7	2.9
FeS	12.9	1.8
Cu_2S	3.5	0.5

A calculation of the equilibrium among FeS, CaO, and C at 900-1100°C identifies the stable products, given in Table 15.

TABLE 15: EQUILIBRIUM PRODUCTS FOR REACTION FeS + CaO + ZC =		
Temperature (°C)	Z (= Moles Carbon)	Major Stable Products
900-1100	1	CO, CaS, Fe
1000	0.5	CO, CO_2, CaS, Fe, FeO
1000	0.01	CO, CO_2, CaS, Fe, FeO

The table shows that sulphide reduction is feasible, with the capture of all sulphur as CaS. The degree of metallization of FeS is dependent upon the quantity of carbon available.

It has been reported[4] that lime typically enhances the kinetics of sulphide reduction significantly. There is some indication which confirms this action in the TGA tests. The earlier initiation of rapid weight loss in lime-bearing charges must be caused by CO and CO_2 discharge at lower temperatures.

8.0 AIR ATMOSPHERE

Graphical results are given in Appendix 3 for tests conducted in air on lime-free calcine charges and on coke alone. An example has been brought forward in this section to illustrate trends, as Figure 7, "Trend Graphs for Series 3 Tests - Air, Atmosphere, No Lime". This has been annotated to show qualitatively the most important effects of the variables.

8.1 Coke Alone

The weight loss curve shows that coke combustion commences at 450°C and proceeds at a nearly linear rate to completion at 1000°C. There is CO_2 evolution throughout this temperature range at a substantially constant rate. The appearance of a CO peak at 500°C is surprising, as oxidation should occur between the coke surface and the inlet of the gas sampling tube.

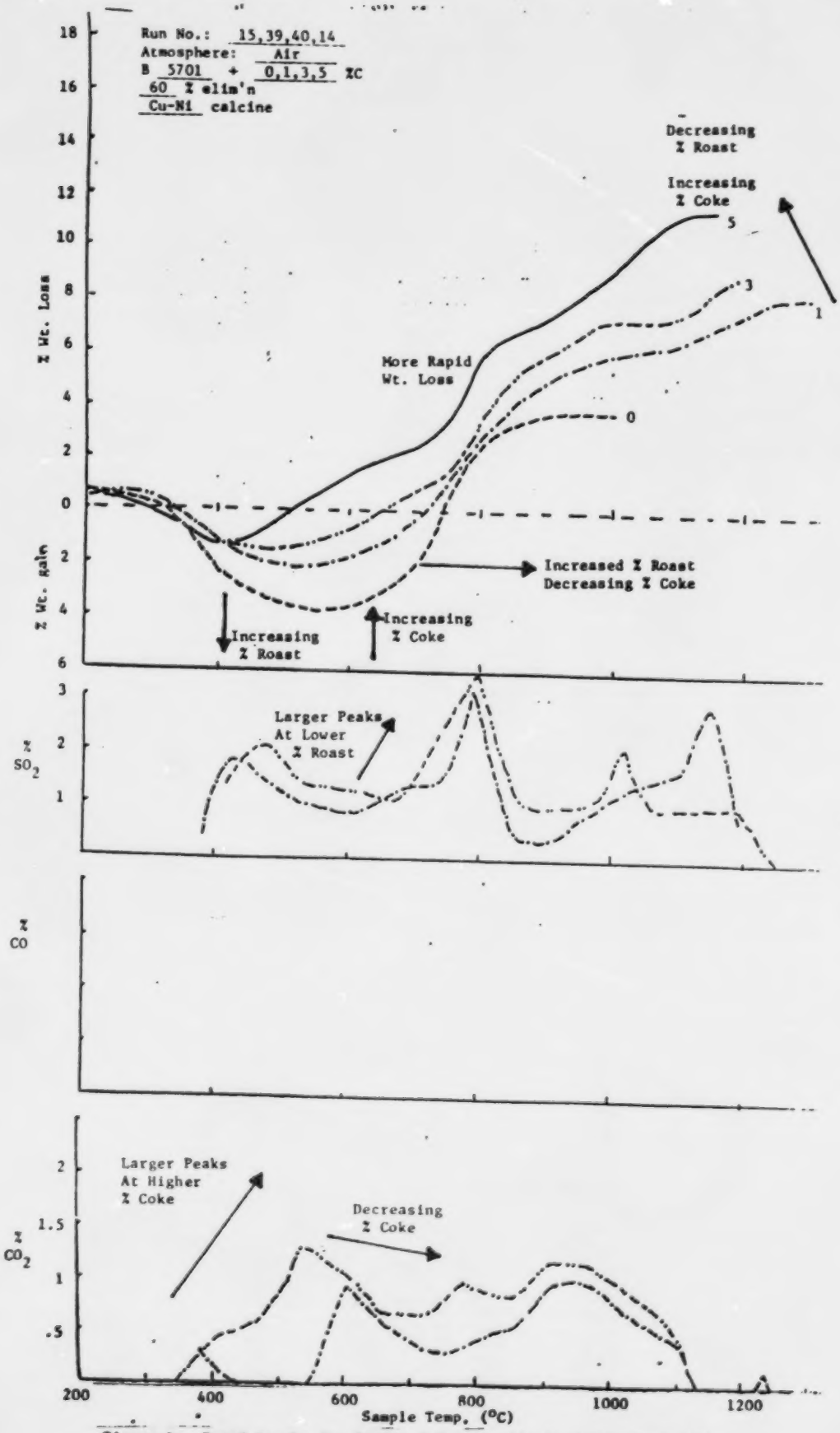

Figure 7: Trend Graphs for Series 3 Tests: Air Atmosphere, No Lime

8.2 Calcine Tests in Air

8.2.1 Characteristic Features

The TGA-GC data for tests performed in an air atmosphere are considerably more complex than for nitrogen. An analysis of all features is not feasible; only the major events and trends will be considered.

(1) Weight Changes:

A small weight loss is recorded up to 300°C, followed by a rapid weight gain. The amount of gain is much larger for samples at high degrees of roast and low coke additions. Also, the transition temperature from weight gain to further loss is much lower at large coke addition levels. A corresponding, but weaker trend exists towards increased transition temperatures at higher degrees of roast. The initial period of weight loss extends to approximately 700-750°C, and is followed by a small region of more rapid loss. At 800-850°C the rate of loss again decreases. There appears to be a strong influence of coke addition levels, particularly associated with the increase from 3% to 5%. At 5% coke there is a much closer coincidence of the curves for different degrees of roast, indicating the dominant influence of coke supply. In addition, the coke dosage has a greater effect on more highly roasted samples.

(2) SO_2 Evolution:

SO_2 is detected throughout the temperature range 400-1200°C, with peaks at approximately 500, 800, and 1150°C. Peak heights are generally larger for less roasted calcines.

(3) CO/CO_2 Evolution:

CO was oxidized in air above the charge and was usually not detected. CO_2 was evolved between 300 and 1200°C, with major amounts at 600°C and 900-1000°C. At higher coke dosages the CO_2 peaks commence at lower temperatures, and are larger.

8.2.2 Postulated Reactions

The same reactions which occur under nitrogen cover also proceed in air. Additional important air-charge reactions impress considerable changes on the behaviour of the system, and will be considered in greater detail.

8.2.2.1 Low Temperature Reactions (<300°C)

The small weight losses in the low temperature range are probably due to drying of free moisture or dehydration of bound water from the calcine. This region is curtailed by the rapid onset of weight gains through sulphate formation.

8.2.2.2 Sulphate Formation (300-680°C)

Weight gains must be caused by oxygen uptake from reactions between solid sulphides and air, with the formation of metal sulphates. The overall reaction is $MeS + 2O_2 = MeSO_4$, but the actual path is more complex, proceeding through oxide and perhaps basic sulphate intermediates. Sulphate formation is favoured by a high partial pressure of SO_3 for the general reaction

$$MeO + SO_3 = MeSO_4$$

In the presence of air, the SO_3 arises from the oxidation of SO_2 evolved during roasting (sulphide-air) reactions.

The metal sulphates of interest here are generally stable below 700°C in the absence of carbon. Relative thermal stabilities with respect to oxides can be allocated by the decomposition pressures listed in Table 6, to form the following order:

$Fe_2(SO_4)$ - least stable
$CuSO_4$
$CuO.CuSO_4$
$NiSO_4$
$CoSO_4$ - most stable

The weight change curves indicate that the formation of sulphates is strongly suppressed by the addition of coke. The diminished stabilities of sulphates in contact with solid coke were previously shown by Table 7, "Equilibrium Products for Carbon-Sulphate Reactions". To examine this phenomenon TGA tests with 0 to 5% coke were arrested at 600°C. Results of chemical analyses are presented in Table 16. These results partly support the TGA data by showing a large decrease in the concentration of sulphates, and particularly copper sulphate, as 1% coke is added to the charge. This result is consistent with the very large difference in weight gains for 0% and 1% coke charges. However, the additional differences in weight gain which are noted as coke addition is raised to 5% are not confirmed by the chemical data, which show no further change in the extent of sulphate formation. The major part of the reduced weight gains at coke additions above 1% must be attributed to coke combustion.

TABLE 16: EFFECT OF % COKE ON SULPHATE FORMATION (Air Atmosphere)

% Roast	% Coke	% Lime	T(°C)	w.s. Ni	w.s. Fe	w.s. Cu	w.s. Co	S	S^{SO4}	w.s. Cu/Ni	w.s. Fe/Ni
67	0	0	600	1.13	0.25	3.06	0.09	6.0	3.1	2.7	0.22
67	1	0	600	0.40	0.40	1.27	0.04	7.4	1.6	3.2	1
67	3	0	600	0.41	0.27	1.41	0.04	7.0	1.6	3.4	0.66
67	5	0	600	0.42	0.06	1.33	0.04	6.3	1.4	3.2	0.14

(w.s. = water soluble)

As the coke content is raised, the ratio of copper:nickel sulphates changes only slightly, but the relative quantity of iron sulphates, expressed by the water soluble Fe:Ni ratio, decreases considerably (the value at 0% coke is inexplicably low). This trend is consistent with the lower stability of $Fe_2(SO_4)_2$ compared with $CuSO_4$ and $NiSO_4$ as the PO_2 value is decreased in the presence of more coke.

From the TGA tests it is evident that the apparent weight gain is greater for more highly roasted samples. Additional tests were carried out at different degrees of roast and arrested at 600°C; chemical analyses are presented in Table 17. According to these results the quantity of sulphates formed depends only slightly on the degree of roast. If a correction is made for the different concentration of sulphates in the original calcines, then the amounts of new sulphate formed are nearly identical for all degrees of roast. The sulphur balance indicates that the amount of sulphur lost during the heating to 600°C is larger at lower degrees of roast. This trend is in accord with expectations for loss of SO_2 by reactions between air and sulphides in the calcine. The relative sizes of SO_2 peaks confirm this. Thus, the behaviour of the system up to about 650°C is controlled by a balance between sulphate formation, SO_2 gas evolution, and coke combustion. At low % roast the sulphide-air reaction is relatively more important than sulphate formation.

TABLE 17: EFFECT OF % ROAST OF CALCINE ON SULPHATE FORMATION (Air Atmosphere)

% Roast	% Coke	% Lime	T(°C)	w.s. Ni	w.s. Fe	w.s. Cu	w.s. Co	S	S^{SO4}	w.s. Cu/Ni	w.s. Fe/Ni
50	0	0	600	0.36	1.38	1.14	0.05	12.5	2.3	3.2	3.8
60	0	0	600	0.45	0.80	1.39	0.04	9.7	1.9	3.1	1.8
75	0	0	600	0.45	0.51	1.73	0.05	5.5	1.9	3.8	1.1

(w.s. = water soluble)

As the degree of sulphur elimination is increased, the composition of the sulphate changes. The ratio of water soluble Cu:Ni remains reasonably constant but the amount of iron sulphate decreases. The greater abundance of iron sulphides at lower % roast indicates that iron sulphate forms more readily from iron sulphide than iron oxide.

8.2.2.3 Solid Sulphide - Air Reactions (350-900°C)

Roasting reactions between air and solid sulphides account for much of the SO_2 release in these tests. The low starting temperatures for substantial SO_2 evolution, less than 400°C, is consistent with the usual values of ignition points of sulphide minerals in air. The first SO_2 peak at approximately 500°C develops from sulphide ignition, then is followed by a sustained high level of discharge.

Reactions are of the type $Cu_2S + 1/2\ O_2 = Cu_2O + SO_2$ where the resultant SO_2 is either released to the gas stream or oxidized to participate in the sulphate formation-decomposition cycle. As expected, the SO_2 strength is much higher than under a nitrogen atmosphere, where the only oxygen resides in the calcine itself. Also included here, is the thermal decomposition of residual unaltered sulphide minerals such as chalcopyrite according to the following reaction:

$$CuFeS_2 = iss + FeS_2$$

Further reaction of the products with oxygen leads to the following overall reaction.

$$4CuFeS_2 + 9O_2 = 2Cu_2S + 2Fe_2O_3 + 6SO_2$$

The greater availability of sulphides at lower degrees of roast is the dominating influence on weight loss and SO_2 evolution. At lower % roast, the sulphide-air reactions commence at slightly lower temperatures and give rise to much higher weight losses and SO_2 discharge. There is also an earlier (lower temperature) change from net weight gain to weight loss in less roasted calcines. This is an indication that the availability of sulphides influences the sulphide-air reaction more than the sulphate formation reactions.

The roasting reactions continue throughout the temperature range of these tests, as long as unreacted sulphides exist. Above 800°C, at higher degrees of roast, the rate of weight loss diminishes sharply as the sulphur in the calcine is depleted. Eventually, all of the charges become totally oxidized in the steady stream of air. Thus, there is no matte formation and the final appearance of the crucible contents is powdery.

In the absence of coke, the balance between SO_2 evolution and sulphate formation determines the weight changes in the system up to 700°C. With coke added the combustion reaction forces a more rapid turnaround from weight gain to loss. It is expected that the competition for oxygen between coke and sulphide should inhibit the roasting reaction at high coke dosages, but the coincident weight loss from coke combustion is impressed upon the curves.

8.2.2.4 Coke-Air Reaction (400-1200°C)

Coke is oxidized at temperatures down to 400°C, but the reaction becomes vigorous at approximately 450°C and proceeds at a high level to 1200°C. For the first (lower temperature) peak the amount of CO_2 evolved is larger and the temperature at which rapid oxidation begins is lower at higher coke addition levels, due to the increased surface area of coke.

There is no apparent effect of the degree of roast. Following the initial CO_2 peak, there is some decrease until the second peak, associated with oxide reduction reactions, appears at 900-1000°C. This reduced CO_2 evolution in the intermediate temperature range, is caused by depletion of coke near the surface of the charge, with the subsequent requirement for gas penetration into the calcine.

The direct combustion of coke which occurs in these tests, imposes a component of weight loss which is independent of the calcine because the mass of carbon lost depends solely upon the amount of coke added to the charge. In evaluating the TGA curves at different coke additions, it must be noted that the difference in weight losses from the calcine is considerably magnified by this effect.

8.2.2.5 Solid State Sulphide-Oxide Reactions

Solid state sulphide-oxide reactions similar to those which are important in tests performed under nitrogen should also be active during the tests in air. It is not possible to discriminate between solid state and gas solid reactions, but it is reasonable to expect that the sulphide-air reaction would be much more rapid.

8.2.2.6 Sulphate Decomposition (700-830°C)

The accelerated weight loss between 750 and 800°C as well as sharp SO_2 peaks centred at approximately 800°C originate from the thermal decomposition of metal sulphates by reactions of the type:

$$1/3\ Fe_2(SO_4)_3 = 1/3\ Fe_2O_3 + SO_3$$

$$SO_3 = SO_2 + 1/2\ O_2$$

As the reactions are similar in air and nitrogen, the discussion presented in Section 6 is applicable.

The effect of temperature on sulphate decomposition was investigated by arrested TGA tests on calcines roasted to 60% sulphur elimination. The chemical analyses given in Table 18 show that the major part of sulphate breakdown occurs between 700 and 800°C. Between 600 and 700°C, the total quantity of sulphates remains constant but the composition becomes iron-poor.

Iron sulphate is less thermally stable than copper and nickel sulphates. At approximately 700°C, the partial pressure of SO_3 above $Fe_2(SO_4)_3$ is sufficiently high for rapid breakdown to Fe_2O_3. Other sulphates, such as $CuO.CuSO_4$ and $NiSO_4$ can continue to form under these condition and then decompose substantially by 800°C.

TABLE 18: EFFECT OF TEMPERATURE ON SULPHATE DECOMPOSITION (Air Atmosphere)

% Roast	% Coke	% Lime	T (°C)	w.s. Ni	w.s. Fe	w.s. Cu	w.s. Co	S	SSO_4	w.s. Cu/Ni	w.s. Fe/Ni
60	0	0	600	0.45	0.80	1.39			1.94	3.1	1.8
60	3	0	700	0.85	0.04	2.05	0.07	7.0	1.98	2.4	0.05
60	3	0	800	0.30	0.01	0.99	0.03	6.1	0.72	3.3	0.03

The concentration of SO_2 detected in the gas stream is greater for charges with a lower coke addition. This trend is consistent with the depressing effect of coke on sulphate formation previously noted in Table 7.

8.2.2.7 Reduction Reaction (850-1200°C)

For the tests conducted in an air atmosphere, the region of very rapid reduction seen in the nitrogen tests is absent. Under the conditions of constant oxygen supply the coke does not act as an effective reductant because it is depleted by combustion before the temperature rises sufficiently for rapid coke-charge reactions.

The TGA curves show that the rate and total amount of weight loss are higher at larger coke additions. Corresponding CO_2 concentrations also follow the same trend. An estimate of the fraction of coke which is directly combusted with atmospheric oxygen in Series 3 is available by examination of the terminal weight losses at 1200°C. By assuming that all of the carbon is burnt in air, the adjusted terminal weight losses are calculated for Table 19.

TABLE 19: TERMINAL WEIGHT LOSSES FOR SERIES 3 ADJUSTED FOR COKE COMBUSTION

	Adjusted Weight Loss (%) at 1200°C			
% Roast	0% Coke	1% Coke	3% Coke	5% Coke
50	7.5	8.5	8.5	8
60	* 4	6.2	6.0	6.5
67	4	5.5	5.5	4.5
75	2.5	3.5	3.5	4

* test terminated at 1000°C

The proximity of values at each degree of roast is a good indication that much of the coke is simply discharged from the system without reacting with the charge.

A second comparison can be made between the final weight losses in Series 3 (air) and Series 1 (nitrogen). Taking unadjusted data in both cases, the values given in Table 20 are obtained.

TABLE 20: COMPARISON OF TERMINAL WEIGHT LOSSES - N_2 AND AIR ATMOSPHERES

% Roast	% Coke							
	5		3		1		0	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
50	16	13	10	13	9	10	8	7.5
60	16	11	10	9	8	8		
67	15	9	11	9	7	6	6	4
75	15	8	11	6	6	4	6	3

In most cases, there is a larger final weight loss for calcine charges heated under nitrogen. The differences become particularly large at high coke dosages and high degrees of roast. Under both air and nitrogen conditions, all of the coke is consumed by conversion to CO_2 and CO. In air, the principal reaction occurs with the atmosphere, removing no oxygen from the charge. Under nitrogen cover, only reduction reactions can occur, with the corresponding weight loss from the calcine. There is an effect of % roast on weight differences in Table 20, caused by the increasing activity of the sulphide-air reaction in the presence of larger quantities of sulphides, i.e. at lower degrees of roast. Thus, the difference in weight change due to oxygen removal from the calcine is increasingly countered by sulphur removal in oxidation or roasting reactions as the % roast is decreased.

8.2.2.8 High Temperature Air-Sulphide Reactions (1000-1200°C)

The increased evolution of SO_2 above 1000°C is indicative of a change to the continuing air-sulphide reactions. There is a corresponding small increase in the rates of weight loss in several cases. Fusion of matte constituents occurs just as the coke is becoming depleted. Liquid sulphides are then in better contact with oxygen, which is decreasingly removed by reaction with carbon.

9.0 CONCLUSIONS

9.1 Summary of Results

The data from this testwork, in conjunction with thermodynamic analysis, have been applied to select the probable sequence of chemical reactions in the heating and fusion stages of electric smelting. These are classified according to the temperature range of occurrence in Figure 8 (nitrogen atmosphere) and Figure 9 (air atmosphere).

Many similar reactions occur under both oxidizing and neutral atmospheres; i.e. drying/dehydration, thermal decomposition of sulphides, sulphide-oxide reactions and sulphate decomposition. With a supply of gaseous oxygen, the interaction of air and charge becomes the dominant feature of the system, through secondary roasting, sulphate formation and coke combustion. High temperature smelting reactions occur in absence of air. These consist primarily of oxide reduction by coke and secondarily, reduction by iron sulphide. Further reactions are indicated if lime is incorporated within the charge, principally SO_2 absorption.

There is substantial overlap of the temperature span of some reactions, with possible confounding of TGA-GC data. In particular, the placement of the weaker, extended reactions, such as solid state sulphide-oxide interactions, is less precise due to the masking effect of more active events.

Figures 8 and 9 also constitute a graphic display of reactions within a vertical section of the charge layer in an electric smelting furnace, showing the series of reaction zones encountered by a unit of charge during its progress from the freeboard to the liquid slag. Heating by slag resistance establishes a temperature gradient, from approximately 500°C at the freeboard to 1230°C at the slag. Thus, low temperature reactions occur partly in contact with ingress air to the furnace. A full range of reactions should appear early in charge heating, but air-charge reactions diminish at greater depth within the bed. The oxygen supply is limited both by the need for diffusion into the charge layer and the increasing reactivity of coke at higher temperatures.

The results from this testwork are highly relevant to electric smelting practice for highly roasted calcines. In the following sections some important aspects will be considered in this context.

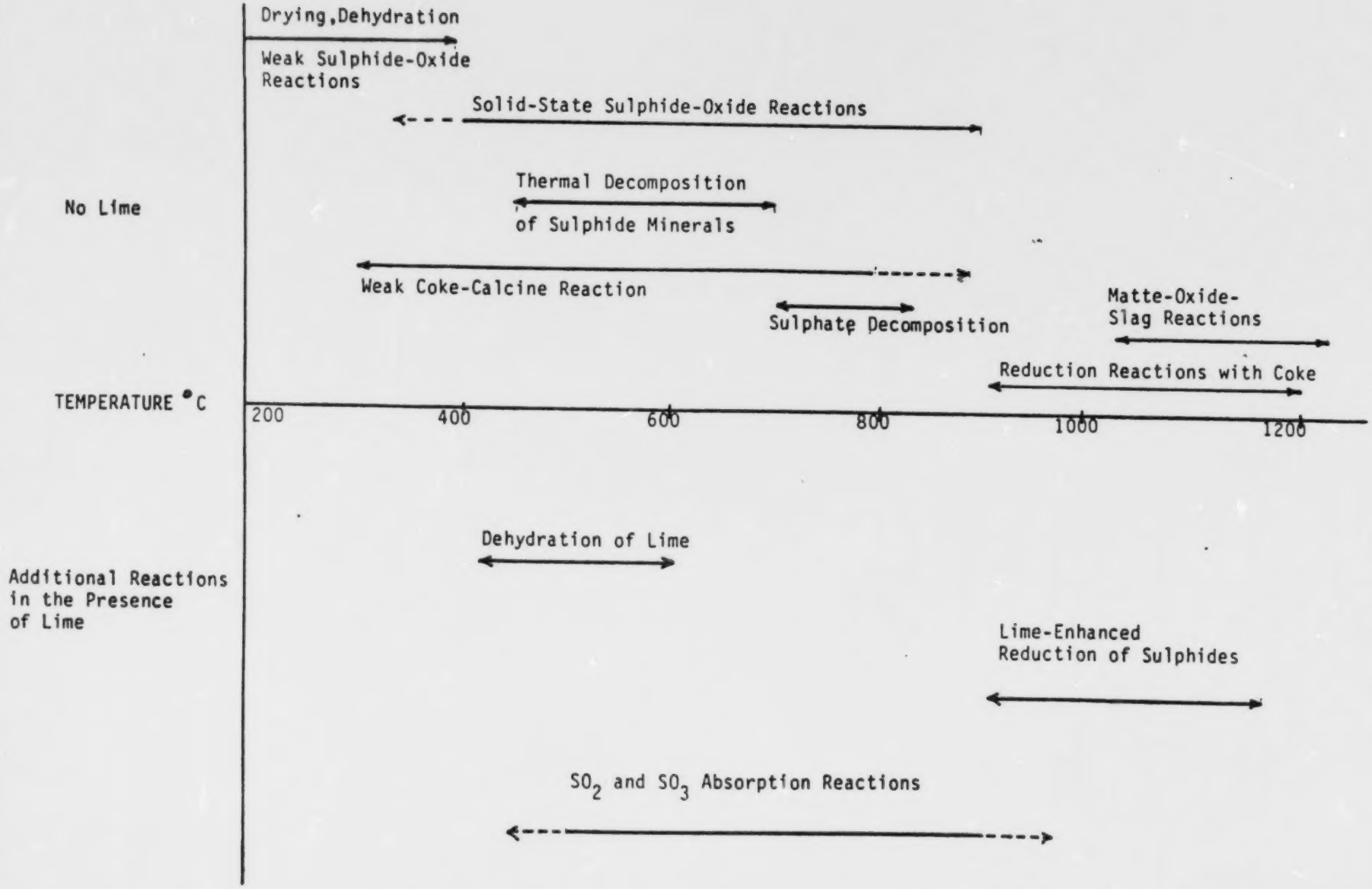

Fig. 8 Temperature Ranges for Reactions : Nitrogen Atmosphere

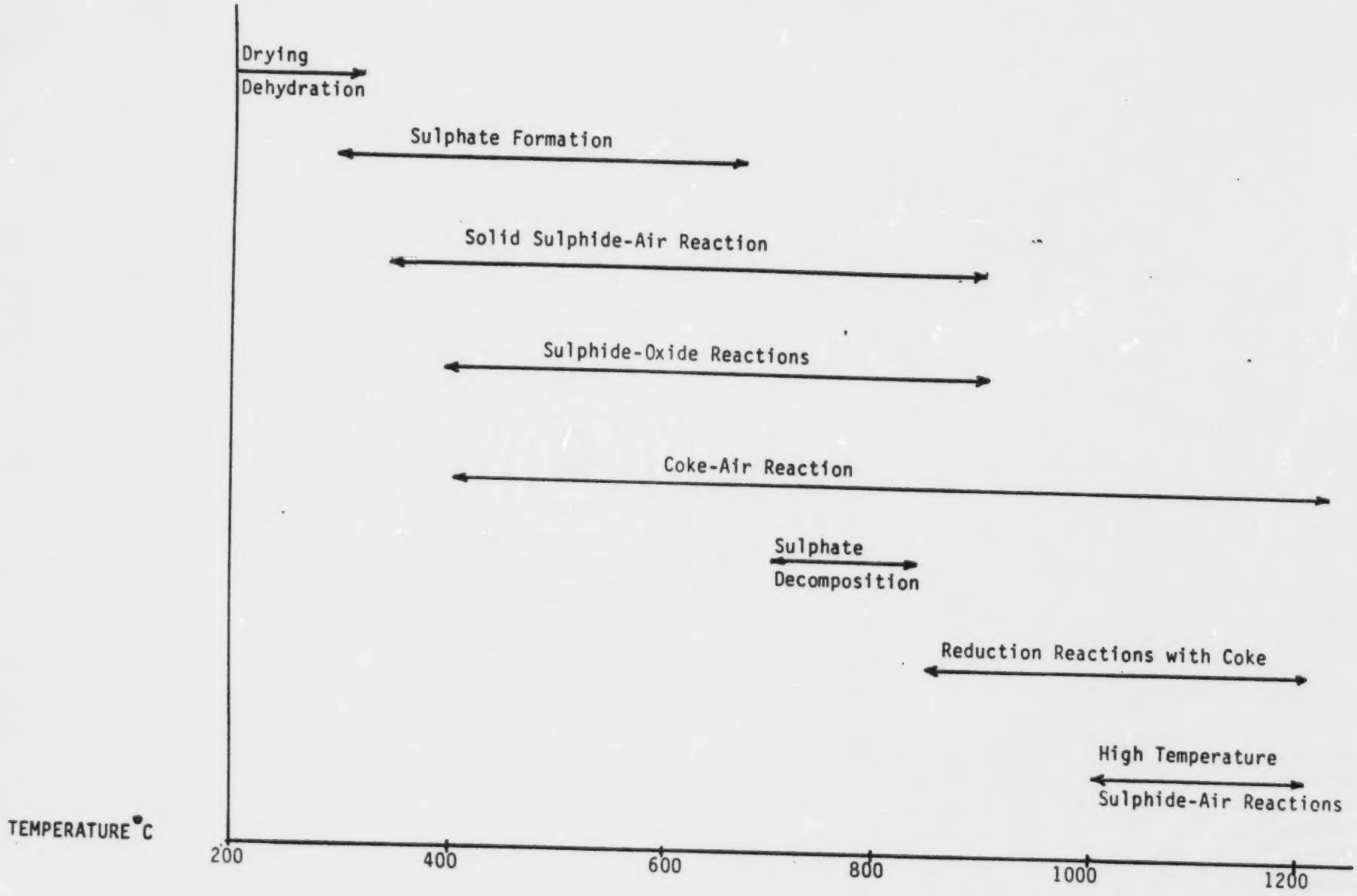

Fig. 9 Temperature Ranges for Reactions : Air Atmosphere

9.2 Degree of Sulphur Elimination

Environmental considerations favour the maximization of sulphur elimination from concentrate prior to electric smelting. Two characteristics of highly roasted calcines have the greatest importance in smelting, lower availability of sulphur and higher input of oxygen.

The sulphur content of calcine affects the release of SO_2 during the charge heating period of smelting. Low strength SO_2 in the offgas is difficult to recover and thus is undesirable. The general trend shown in the experimental work was the inverse relationship between the volume of SO_2 and the degree of sulphur elimination from calcine by prior roasting. Each of the SO_2-producing reactions is influenced by a lower sulphur content in the calcine.

Increased desulphurization is achieved by roasting concentrates at higher temperatures. Under these conditions, the kinetics of mineral decomposition are faster and a larger part of the labile sulphur is removed. Higher temperature roasting also depresses the formation of metal sulphates in the calcine. These original sulphates contribute directly to SO_3 and SO_2 formation in the electric furnace by undergoing thermal decomposition. Any decrease in sulphate formation in the roasters is beneficial both in terms of lower SO_2 formation and lower oxygen input to smelting.

Air-sulphide or secondary roasting reactions occur to an extent which is determined by sulphide and oxygen supply. The lesser abundance of mineral sulphides in highly roasted calcines presents a lower surface area for these reactions and decreases SO_2 formation. Since these reactions depend upon the diffusion of oxygen into the charge, SO_2 formation would be depressed by features which inhibit this supply, such as operation with a deeper calcine layer.

In the fusion temperature region, the smelting chemistry is sensitive to both the extra oxygen input and reduced sulphur content of highly roasted calcines. The mass of matte formed is diminished by the limited availability of sulphur and the preferential distribution of oxidized iron to the slag. Thus, a smaller quantity of higher grade matte forms when highly roasted calcines are introduced. Concurrently, valuable metals (Co, Ni, Cu) are also partly oxidized to slag, presenting the requirement for the addition of a reductant.

9.3 Utilization of Coke

Consistent with the overall objective of smelting more highly roasted calcines, it is necessary to provide more reduction capacity to recover valuable metal oxides from slag. The coke added to the charge may react in various ways, some of which are unproductive. Substantial coke burnoff can occur through contact with ingress oxygen at temperatures above 300°C. Direct coke combustion is disadvantageous in two ways. First, there is wastage of coke and diminished availability for metal oxide reduction. Second, the combustion of carbon monoxide in the furnace freeboard may cause unacceptably high temperatures. The latter reason constitutes a practical limitation on coke feedrate.

Below the fusion temperature, other reactions involving coke are less important than direct combustion. Solid state reduction is slow, but some reduction of sulphates can occur. This reaction also consumes carbon, but is not functionally required because of the inevitable thermal decomposition of these sulphates at higher temperatures.

The conceptual requirement to obtain higher coke utilization is for a reductant with sufficiently low reactivity at lower temperatures, to inhibit combustion. Different coke types or granulometry may be effective for this purpose.

Productive coke involvement in electric smelting is primarily in the matte-assisted reduction of oxides. These reactions are very rapid and may be tolerant of different coke feeds. High temperature smelting reactions are limited by coke supply, up to the 5% addition level. Reductant consumption within this regime is complete and rapid.

If a greater degree of reduction is achieved, the metal saturation constraint could be reached. The reduction of excessive quantities of iron into matte can cause furnace operating problems by precipitation of an alloy which accretes in the hearth.

9.4 Lime Addition

The outstanding consequence of lime addition to the charge is the suppression of SO_2 release during smelting. At high degrees of roast of calcine, such as 67%, the SO_2 capture is nearly complete at lime dosages from 5% to 15%. The stable sulphur-bearing compound under reducing conditions is CaS, though $CaSO_4$ may also exist.

The primary benefit of lime addition is the absorption of SO_2 evolved from the reactions in the charge heating temperature range, up to 950°C. At higher temperatures, the reduction reactions may be enhanced by lime. Earlier, more rapid reaction was noted in the testwork, but there was little effect on the final results.

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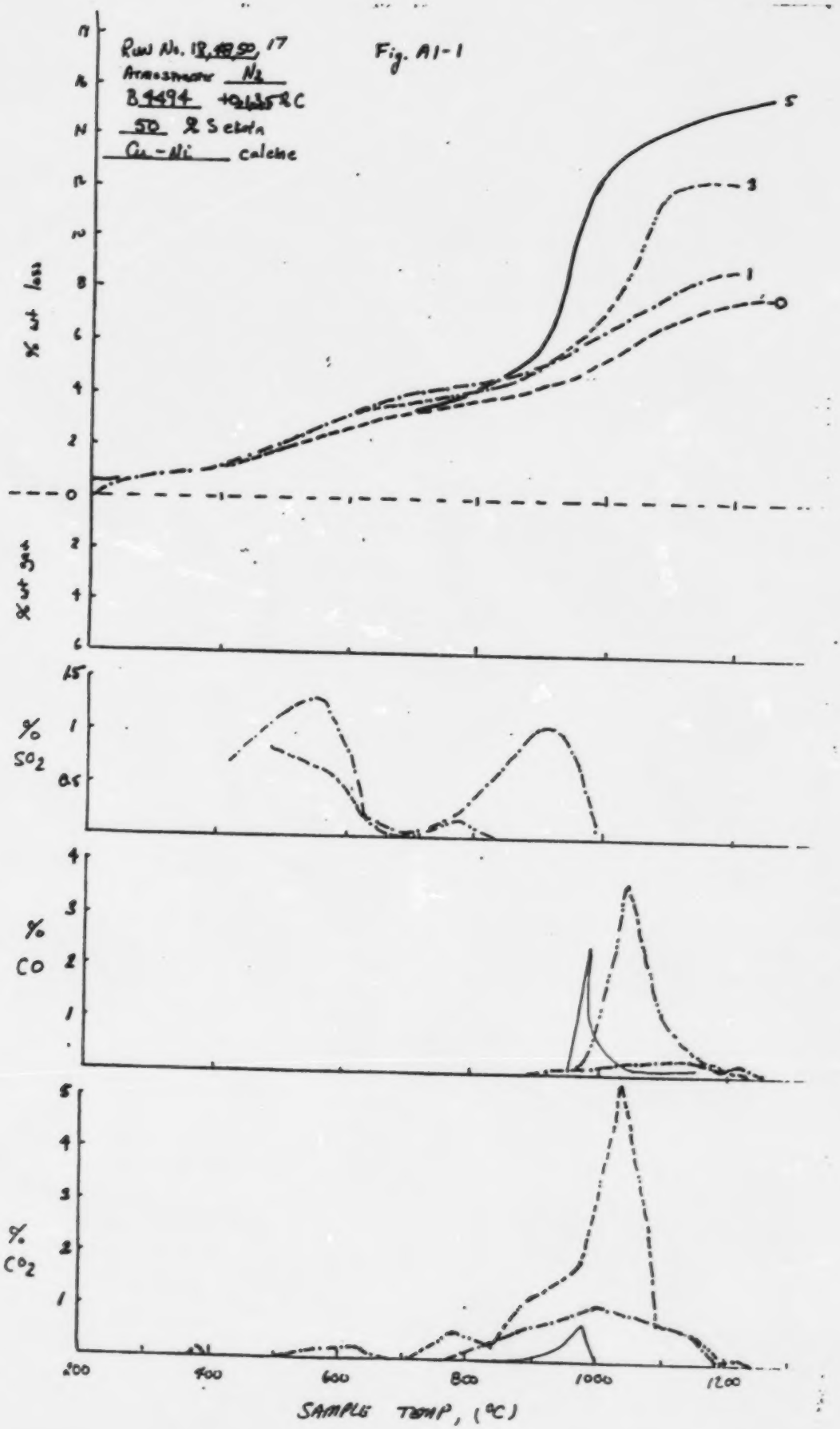
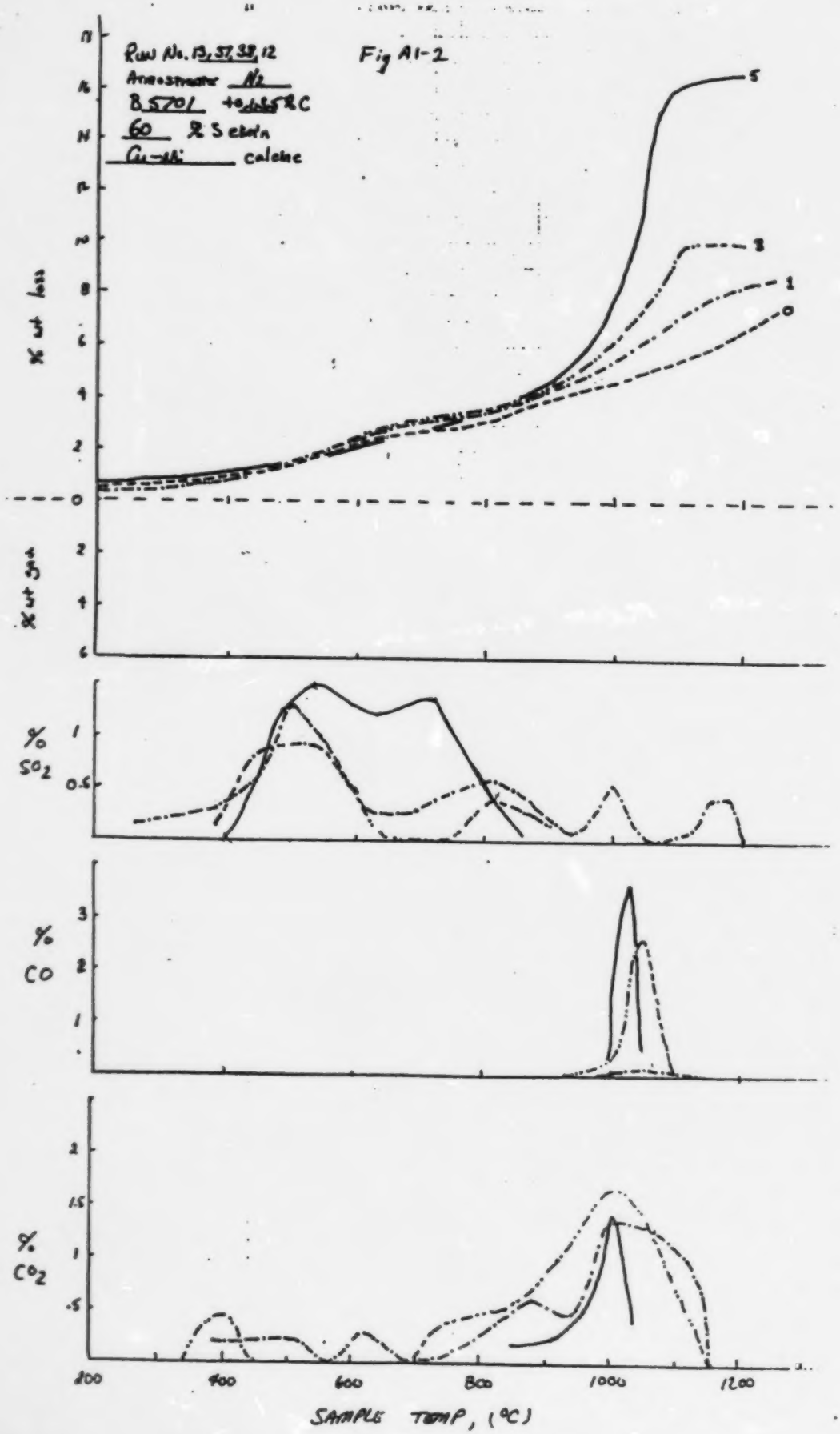
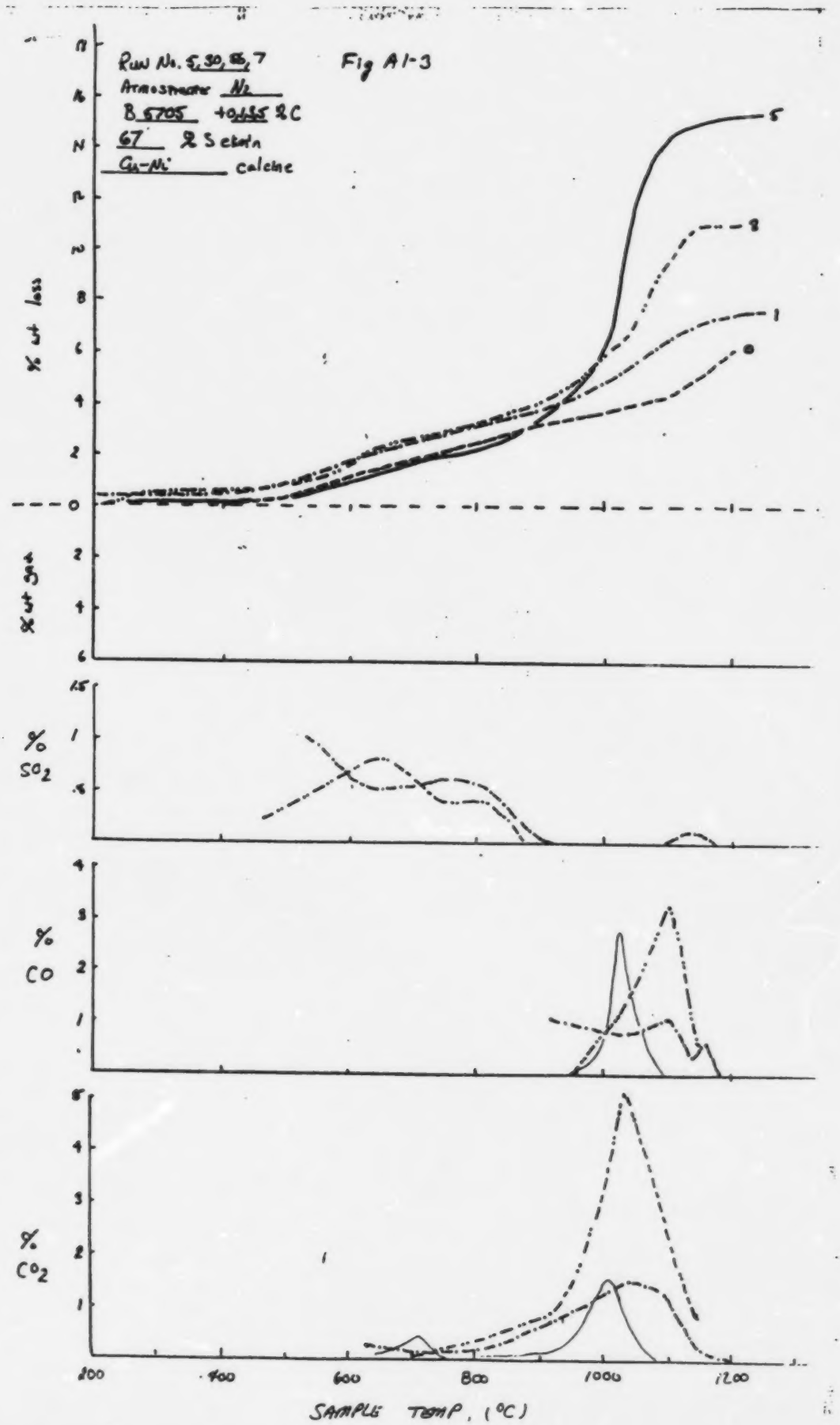
APPENDIX 1

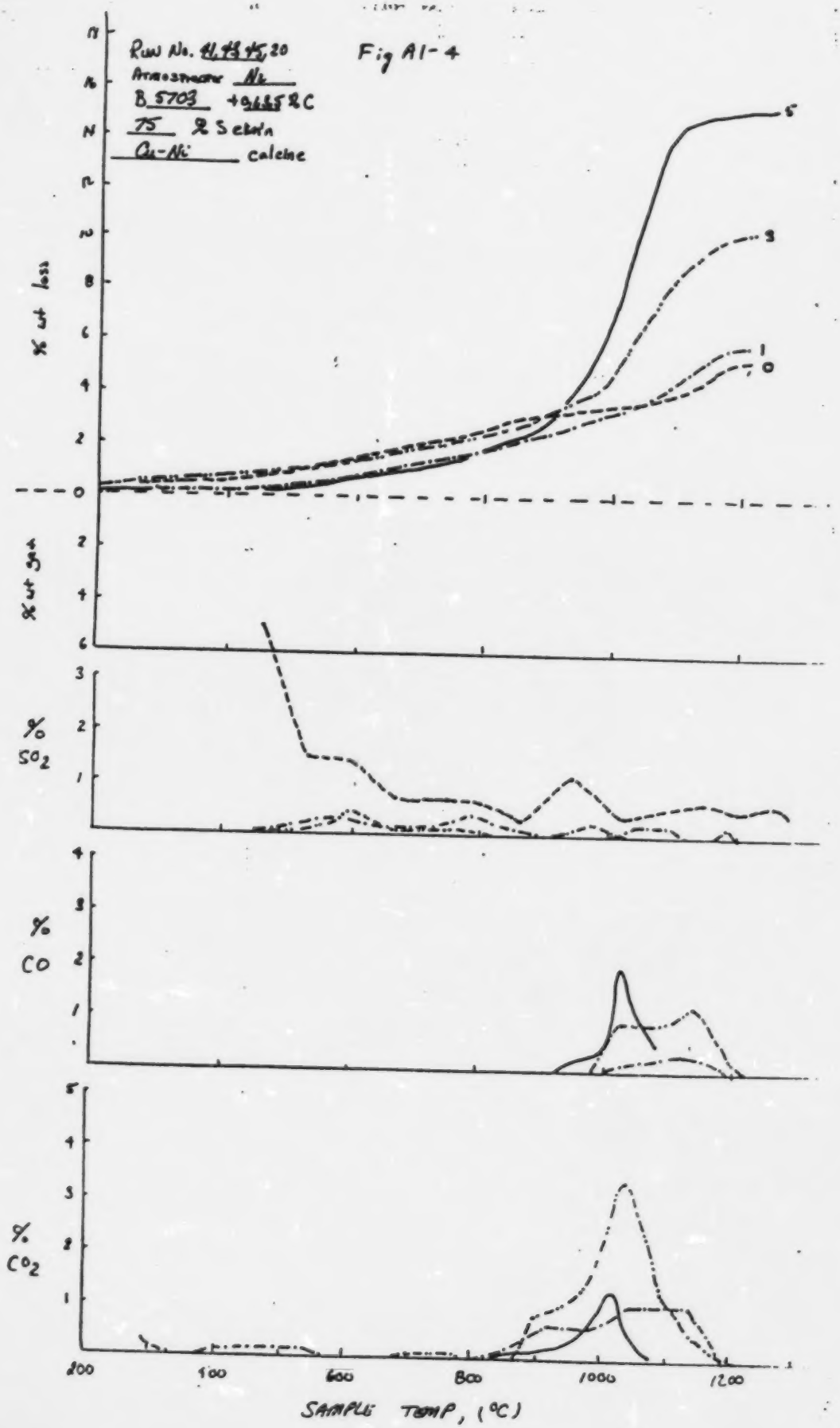
GRAPHICAL RESULTS FOR TEST SERIES 1: NITROGEN ATMOSPHERE, NO LIME

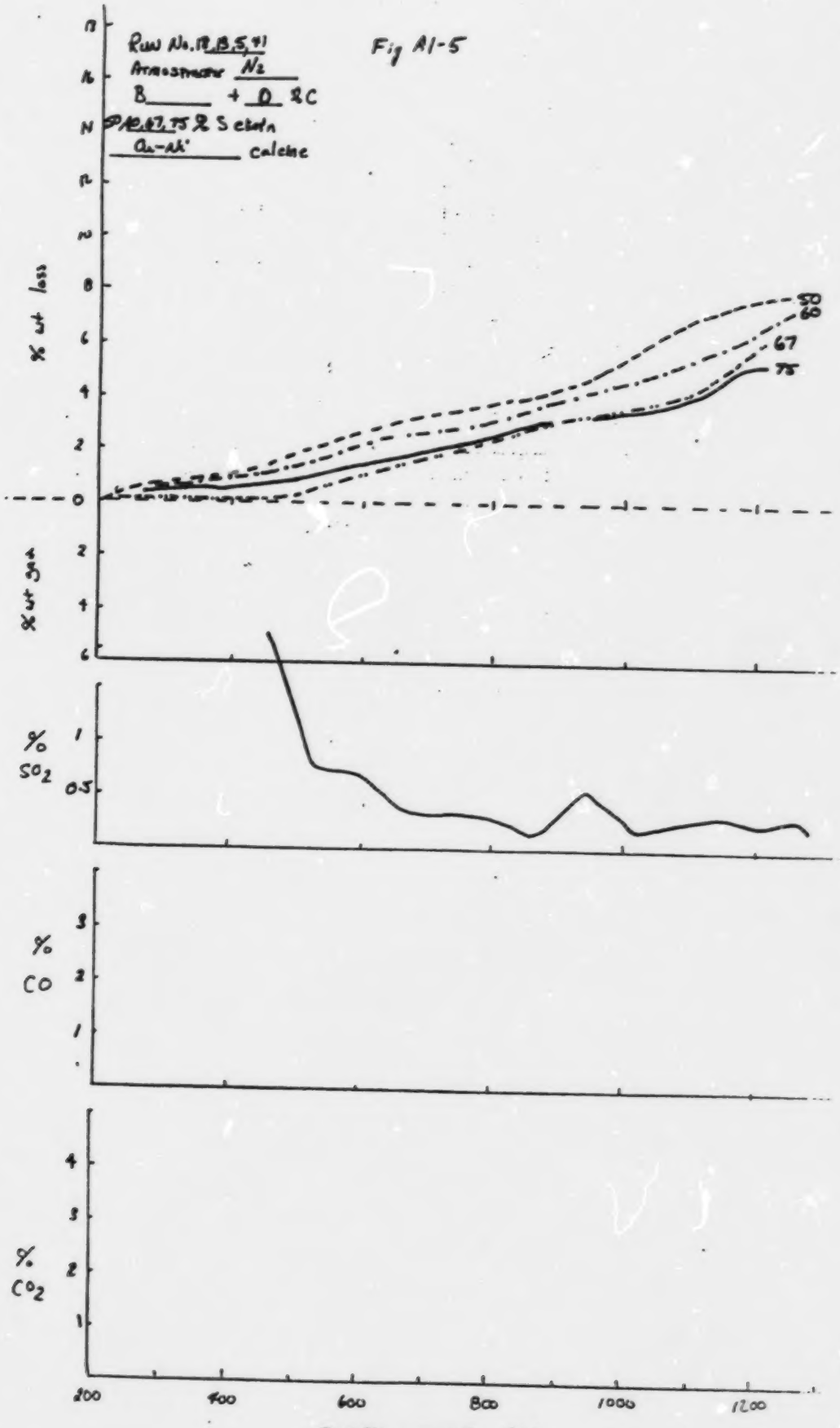
Fig. No.	% Roast of Calcine	% Coke Addition
A1-1	50	0-5
A1-2	60	0-5
A1-3	67	0-5
A1-4	75	0-5
A1-5	50-75	0
A1-6	50-75	1
A1-7	50-75	3
A1-8	50-75	5

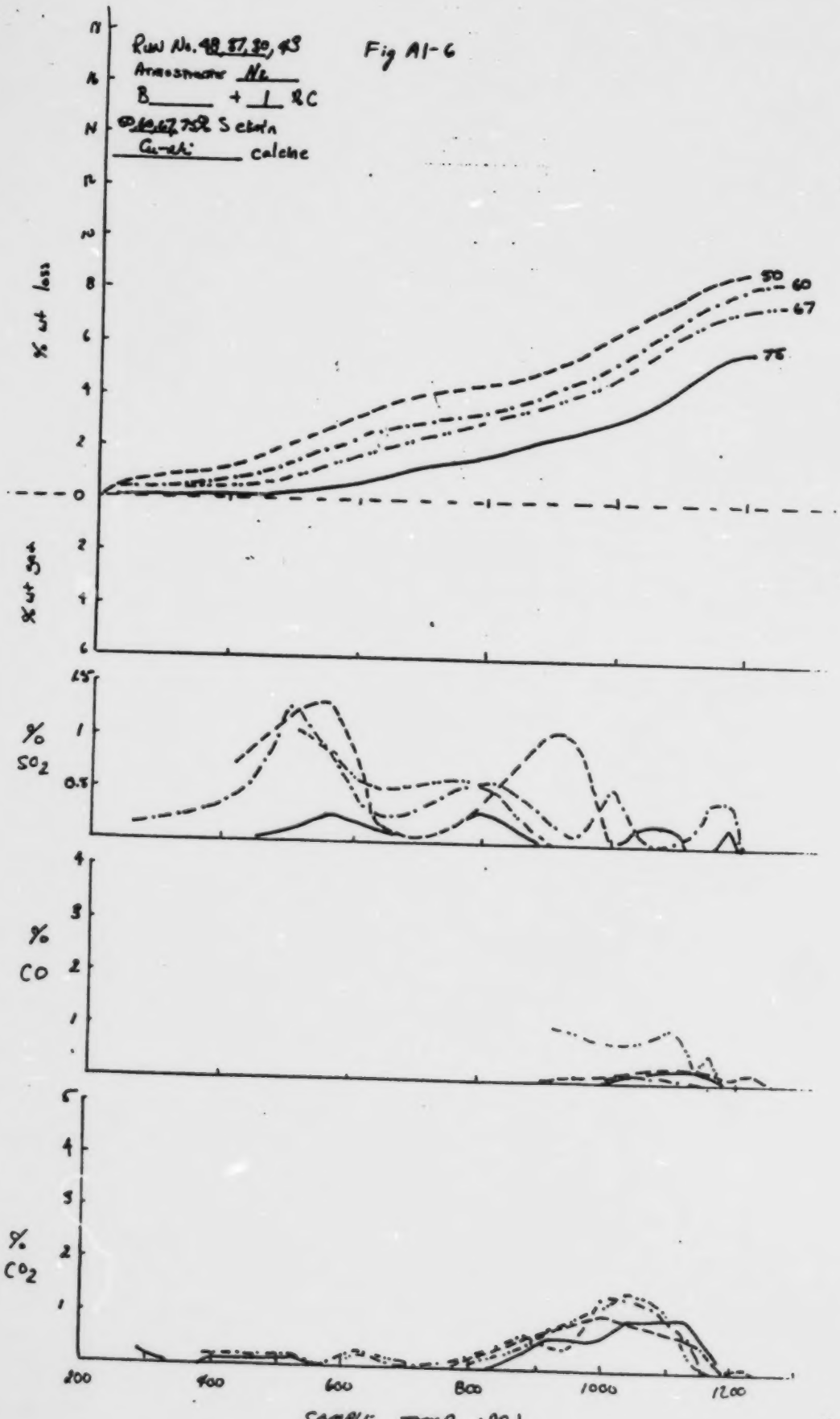

Run No. 18, 19, 20, 17
Atmosphere N2
8.9494 +0.1355 gC
50 % Selain
Cu - Ni calcine
Fig. A1-1
% wt loss
% wt gain
% SO2
% CO
% CO2
SAMPLE TEMP, (°C)
200
400
600
800
1000
1200

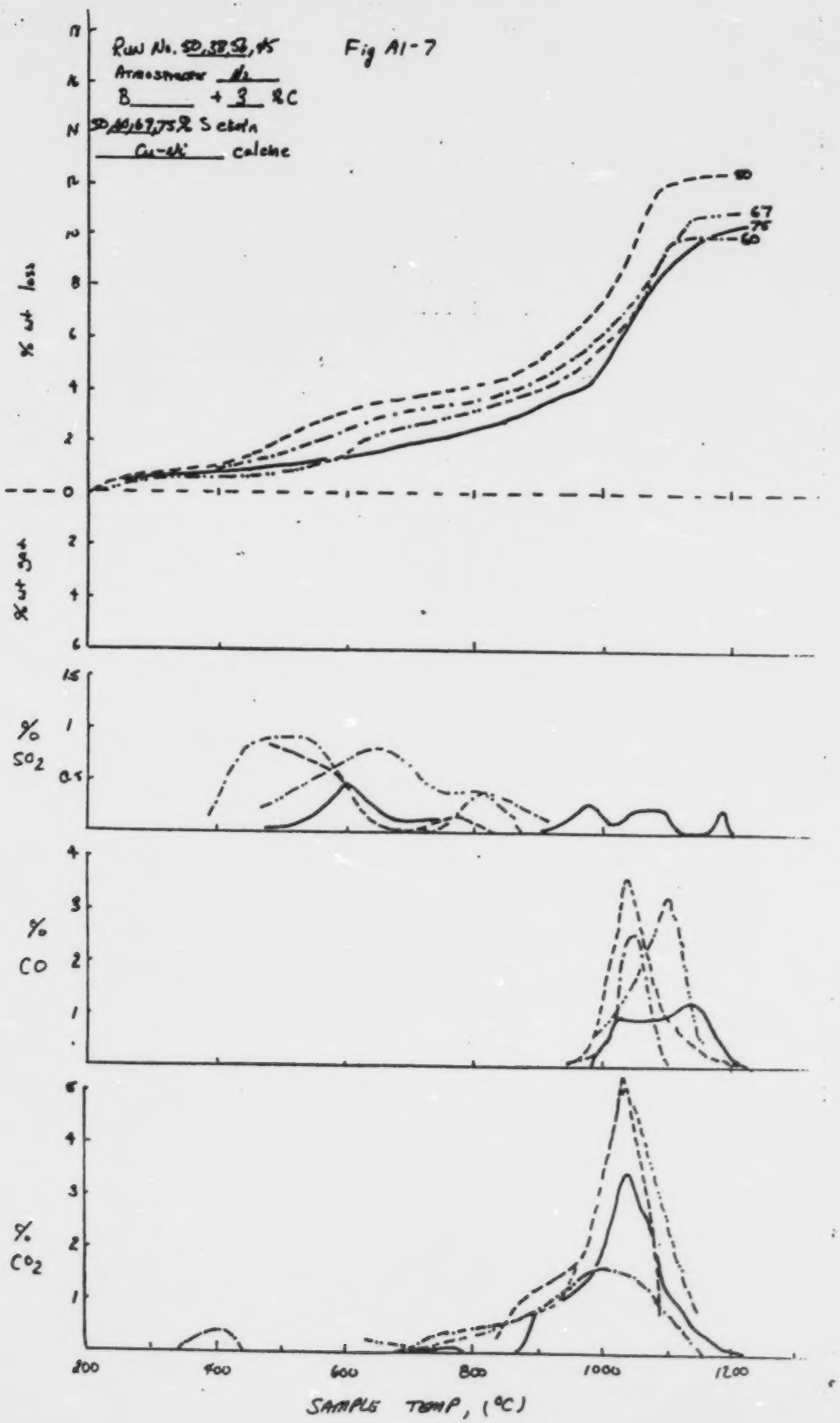

Run No. 13, 37, 38, 12
Atmosphere N2
8.5701 +0.065 RC
60 % Sebain
Cu-Ni calcine
Fig A1-2
% wt loss
% wt gain
5
3
1
0
% SO2
% CO
% CO2
200
400
600
800
1000
1200
SAMPLE TEMP, (°C)

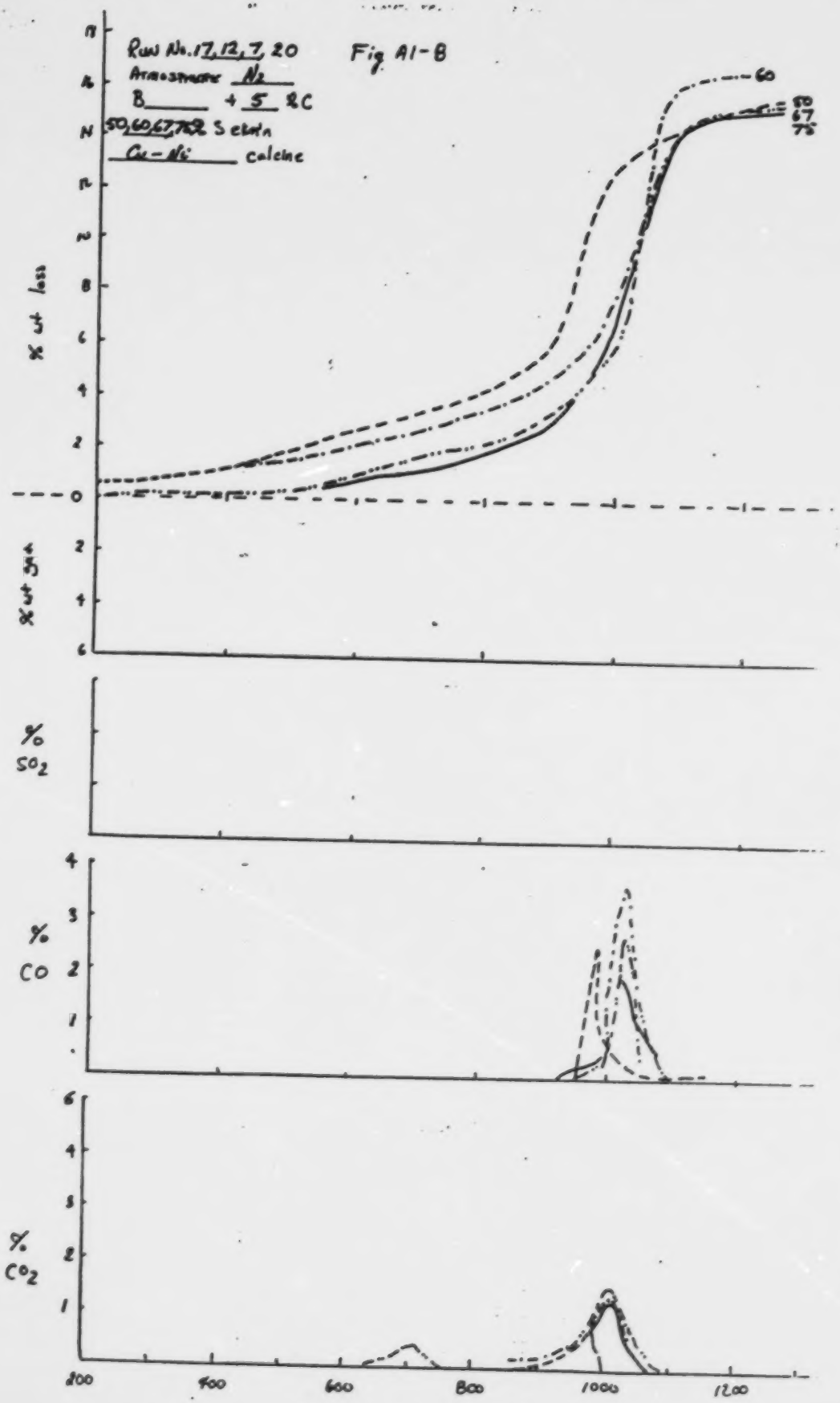

Run No. 5, 30, 55, 7
Atmosphere N2
B 5705 +0.155 2C
67 2 Sebdn
Cu-Ni calcine
Fig A1-3
% wt loss
% wt gain
% SO2
% CO
% CO2
SAMPLE TEMP. (°C)


Run No. 41,43,45,20
Atmosphere N2
B 5703 +0.625 %C
75 % Sebkha
Cu-Ni calcine
Fig A1-4
% wt loss
% wt gain
% SO2
% CO
% CO2
5
3
1
0
100
400
600
800
1000
1200
SAMPLE TEMP, (°C)


Run No. 19,B,5,91
Fig A1-5
Atmosphere N2
B ____ + D 2C
SP 10,67,75 2 S clatn
Cu-Ali calcine
% wt loss
% wt gain
% SO2
% CO
% CO2
50
60
67
75
SAMPLE TEMP, (°C)


Run No. 48, 57, 50, 43
Atmosphere N2
B ____ + 1 %C
Sclera
Cu-ch: ____ caliche
Fig A1-6
% wt loss
50
60
67
75
% wt gain
% SO2
% CO
% CO2
200
400
600
800
1000
1200
SAMPLE TEMP, (°C)


Run No. SD,SB,SA,45
Atmosphere N2
B ____ + 3 %C
SD 60,67,75% S etc in
Cu-Ni calcine
Fig A1-7
% wt loss
% wt gain
80
67
75
60
% SO2
% CO
% CO2
200
400
600
800
1000
1200
SAMPLE TEMP, (°C)


Run No. 17, 12, 7, 20
Atmosphere N2
B ____ + 5 %C
50, 60, 67, 75 Sec/min
Cu-Ni calcine
Fig A1-B
% Wt loss
% Wt Gain
60
50
67
75
% SO2
% CO
% CO2
100
400
600
800
1000
1200
SAMPLE TEMP, (°C)

APPENDIX 2

GRAPHICAL RESULTS FOR TEST SERIES 2: NITROGEN ATMOSPHERE, 0-15% LIME ADDITION

Fig. No.	% Roast	% Coke	% Lime
A2-1		Lime only	
A2-2	60	5	0-15
A2-3	67	5	0-15
A2-4	60	5	0-15] adjusted for
A2-5	67	5	0-15] moisture in lime

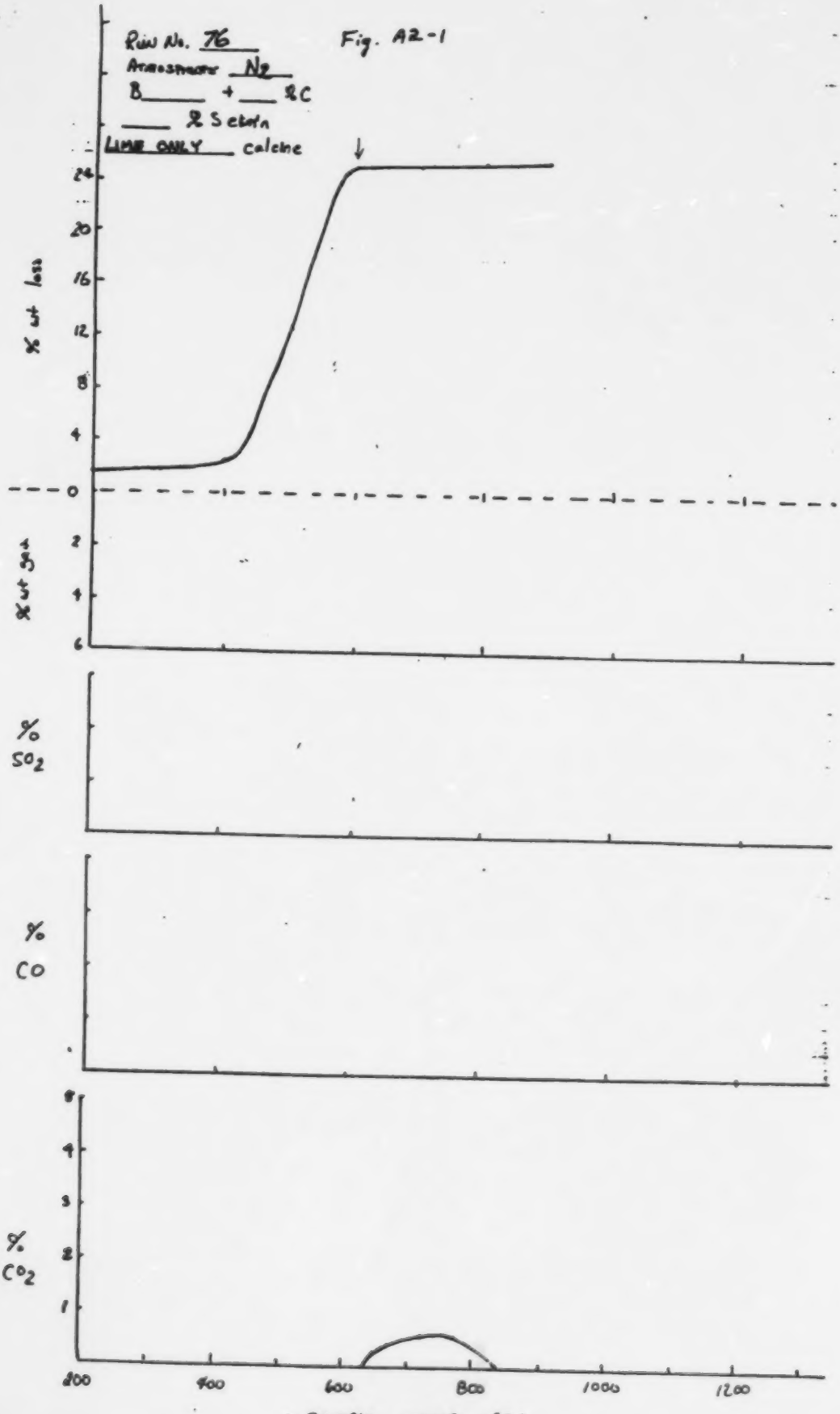
Run No. 76 Fig. A2-1

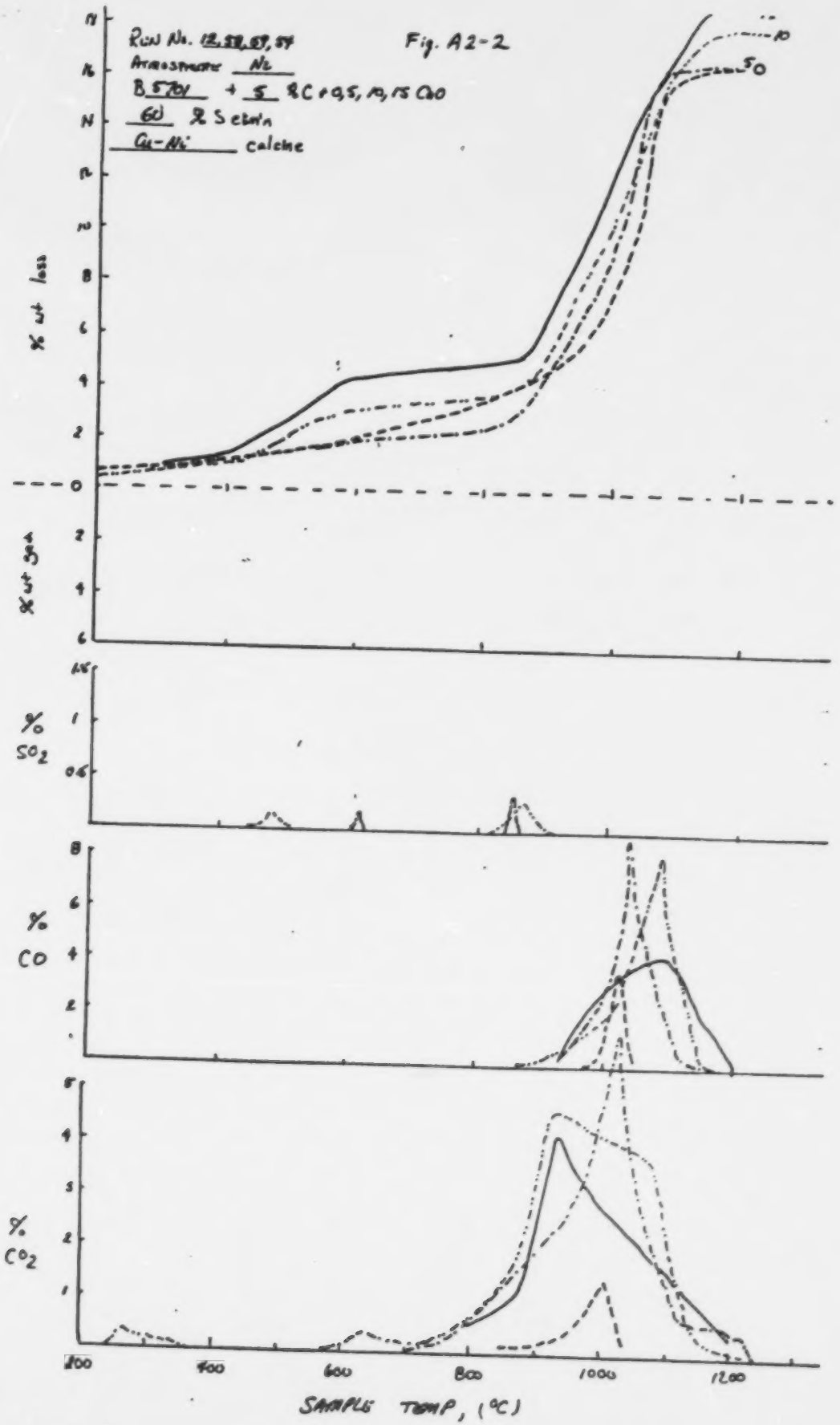
Atmosphere N2

B____ + ___ %C

___ % Sebatn

LIME ONLY ___ calcine




Run No. 12, 28, 57, 84
Fig. A2-2
Atmosphere N2
B 5 70V + 5 %C + 0.5, 10, 15 CaO
60 % Sieve in
Cu-Ni calcine
10
50
% wt loss
% wt gain
% SO2
% CO
% CO2
SAMPLE TEMP, (°C)

Run No. 2.3%.89.61 Fig. A2-3
Atmosphere N₂
B 5705 + 5 %C + 0,5,10,15 %CaO
67 % Sebrin
Ca-silicate calcine

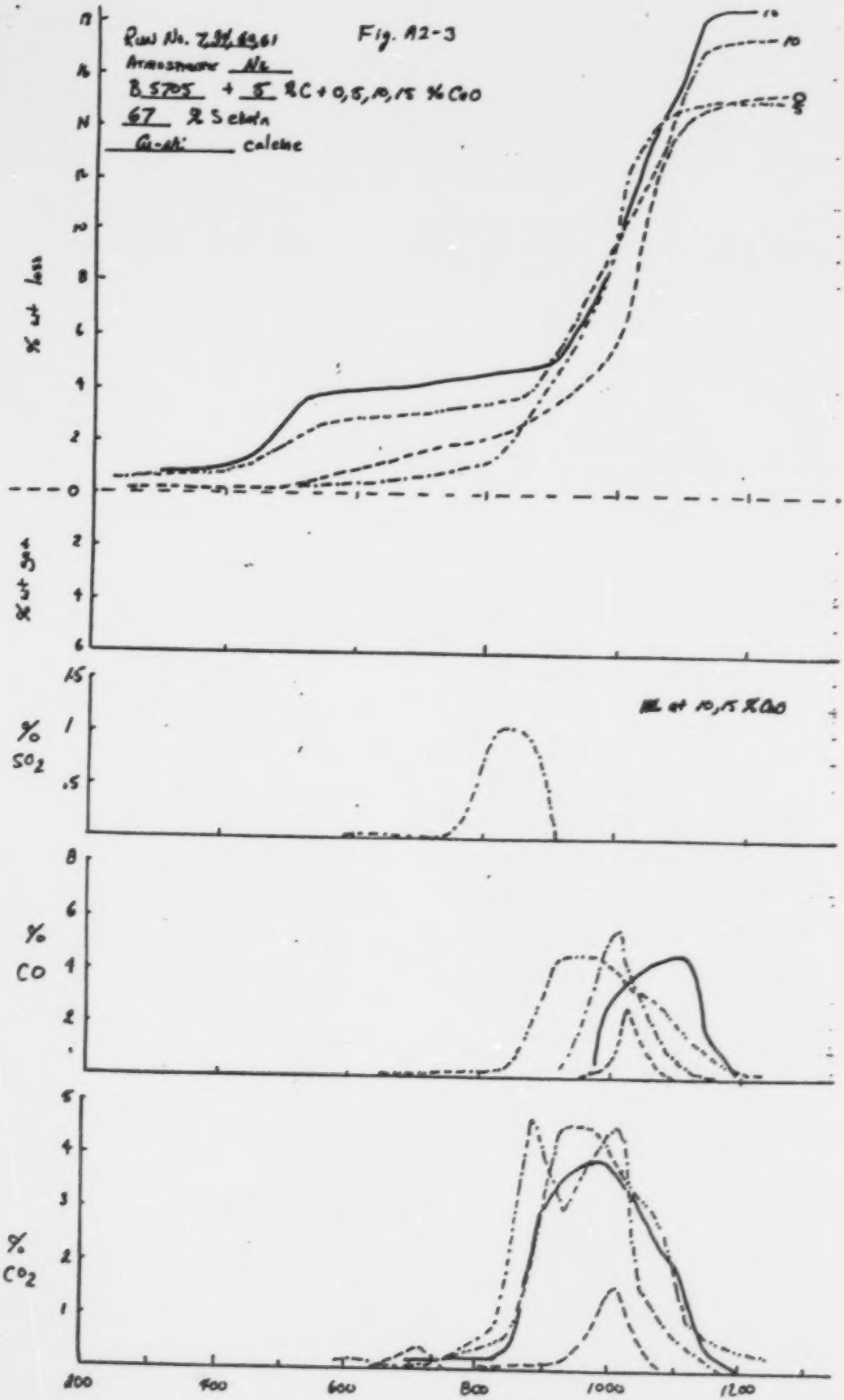


Fig. A2-4

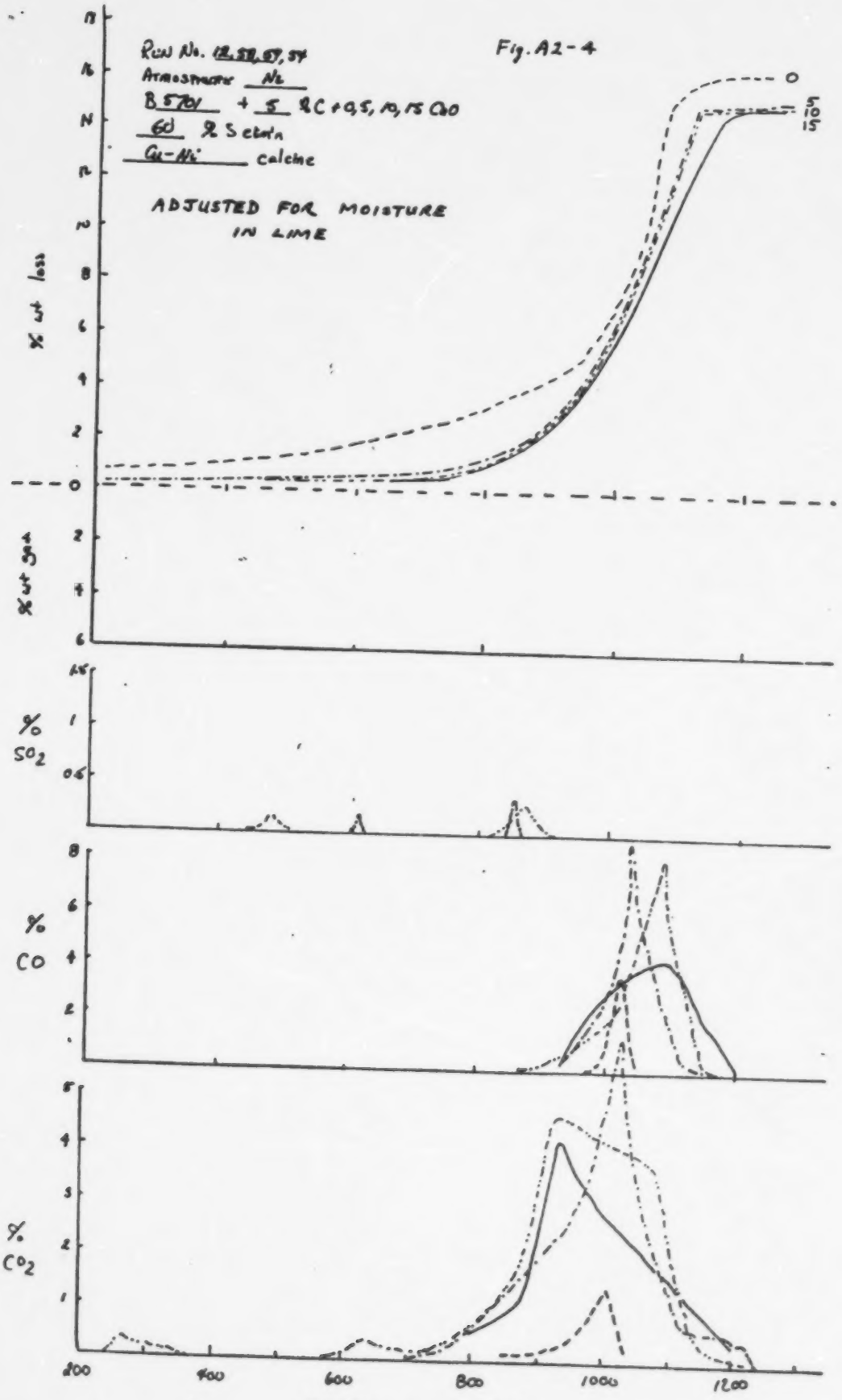
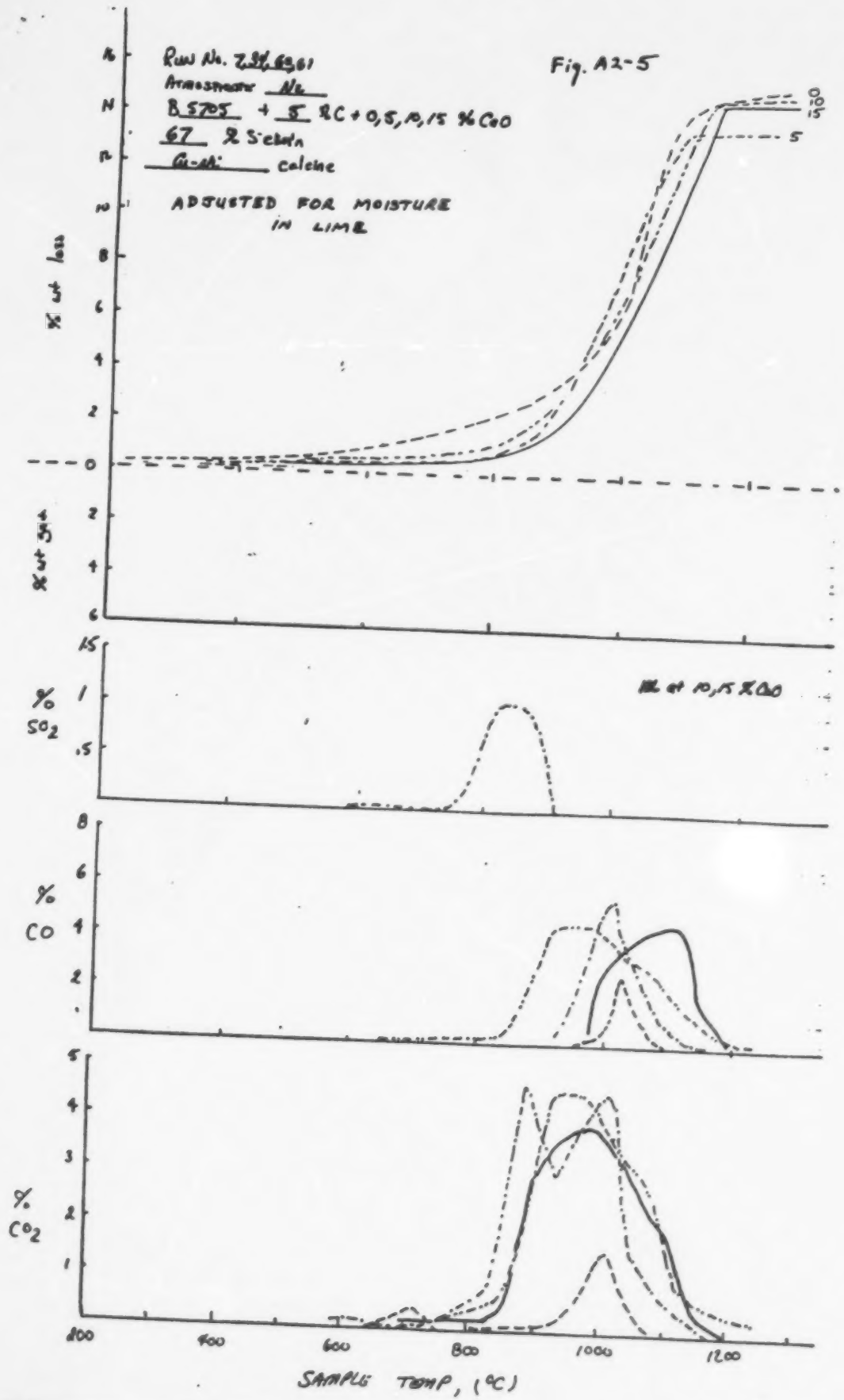

Run No. 12, 58, 57, 54
Atmosphere N2
B 5701 + 5 % C + 0, 5, 10, 15 CaO
60 % Sctn'n
Cu-Ni calcine
ADJUSTED FOR MOISTURE IN LIME
% wt loss
% wt gain
0
5
10
15
% SO2
% CO
% CO2
200
400
600
800
1000
1200
SAMPLE TEMP, (°C)

Fig. A2-5


Run No. 7.5%.69.61
Atmosphere N2
B.5705 + 5 %C + 0,5,10,15 % CaO
67 % Silicon
Ca-Al- calcine
ADJUSTED FOR MOISTURE IN LIME
% wt loss
% wt gain
0
5
10
15
% SO2
% CO
% CO2
SAMPLE TEMP, (°C)
100
400
600
800
1000
1200

APPENDIX 3

GRAPHICAL RESULTS FOR TEST SERIES 3: AIR ATMOSPHERE

Fig. No.	% Roast of Calcine	% Coke Addition
A3-1	Coke only	
A3-2	50	0-5
A3-3	60	0-5
A3-4	67	0-5
A3-5	75	0-5
A3-6	50-75	0
A3-7	50-75	1
A3-8	50-75	3
A3-9	50-75	5

Run No. 9, 23

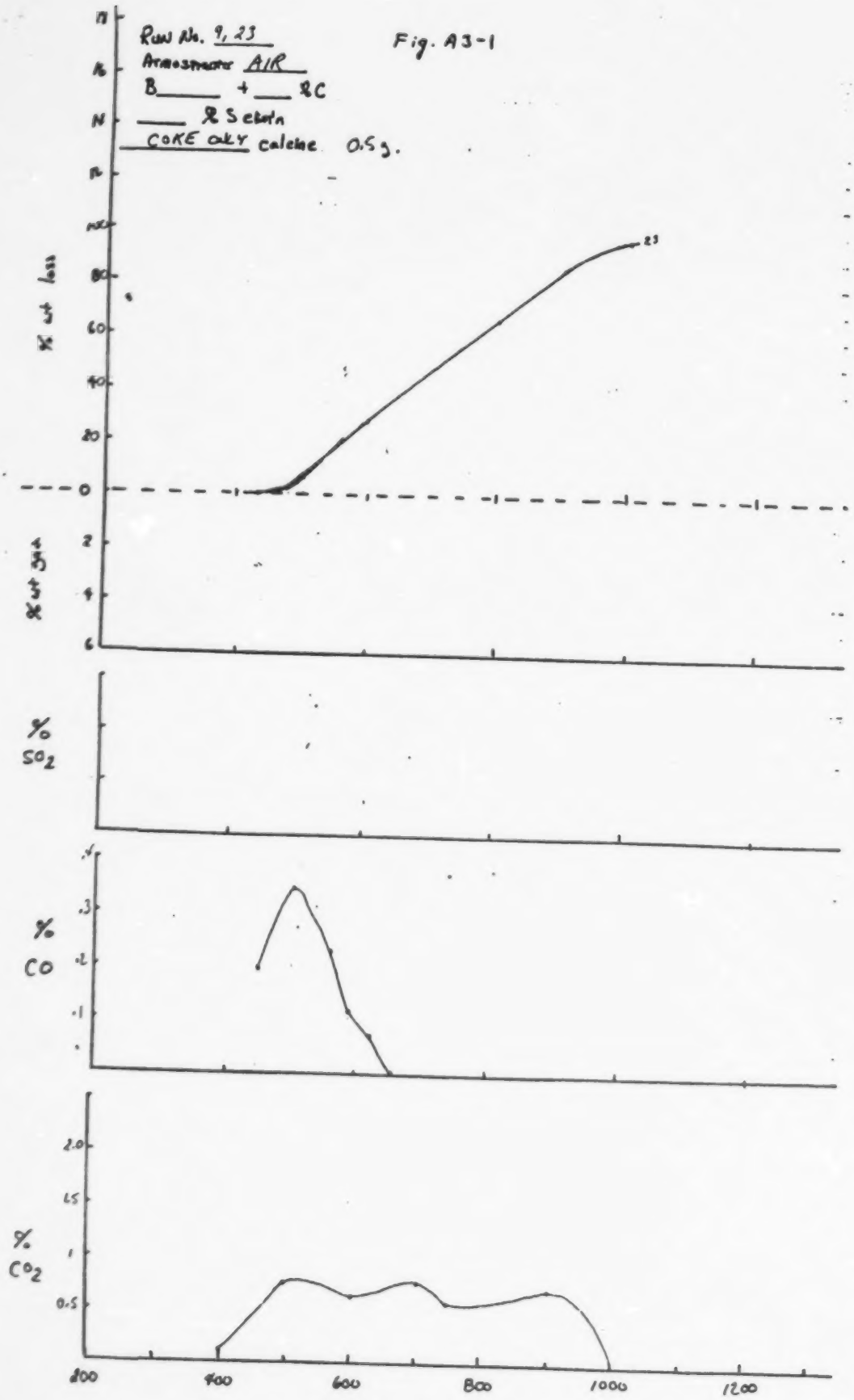
Fig. A3-1

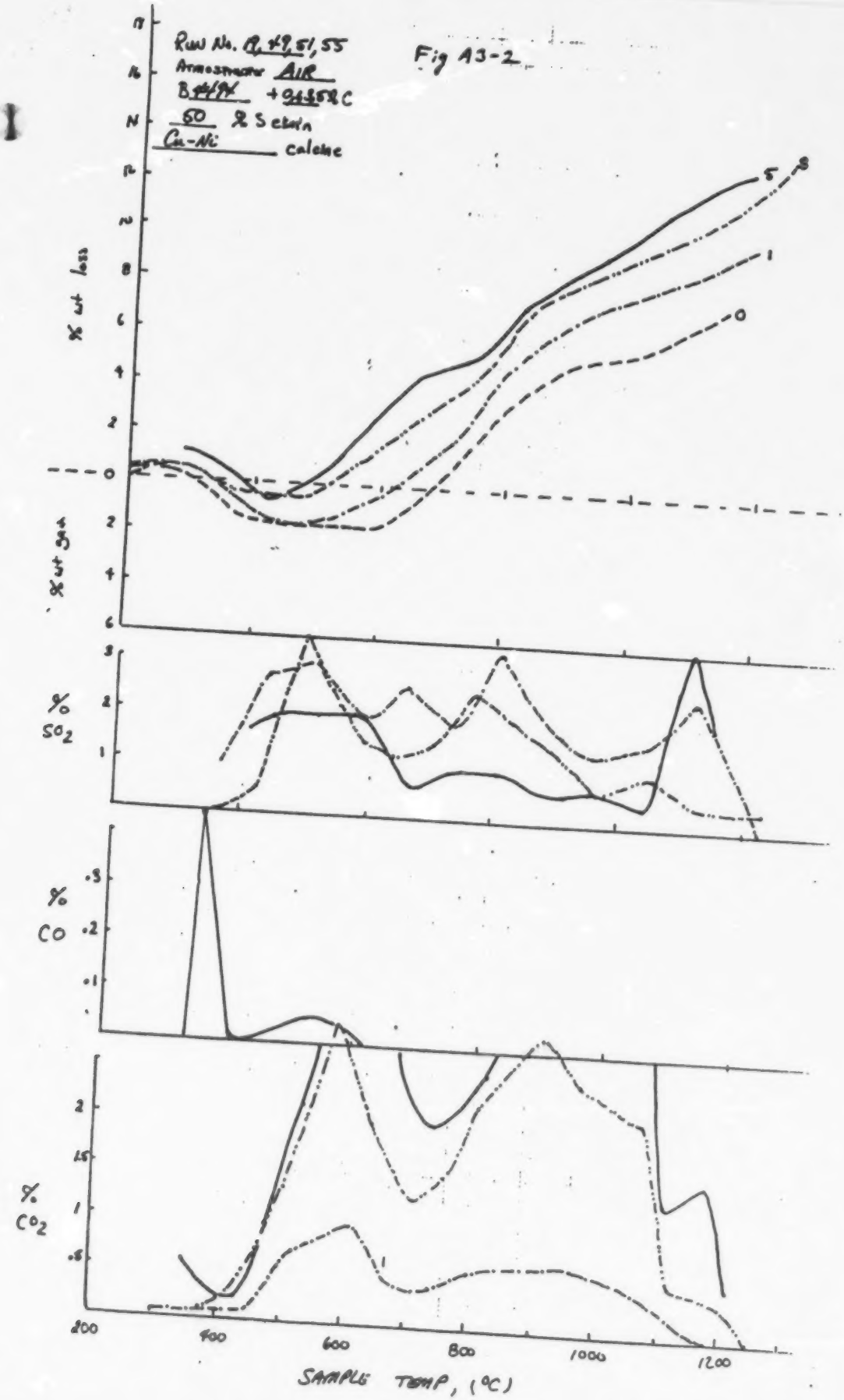
Atmosphere AIR

B_____ + ___ %C

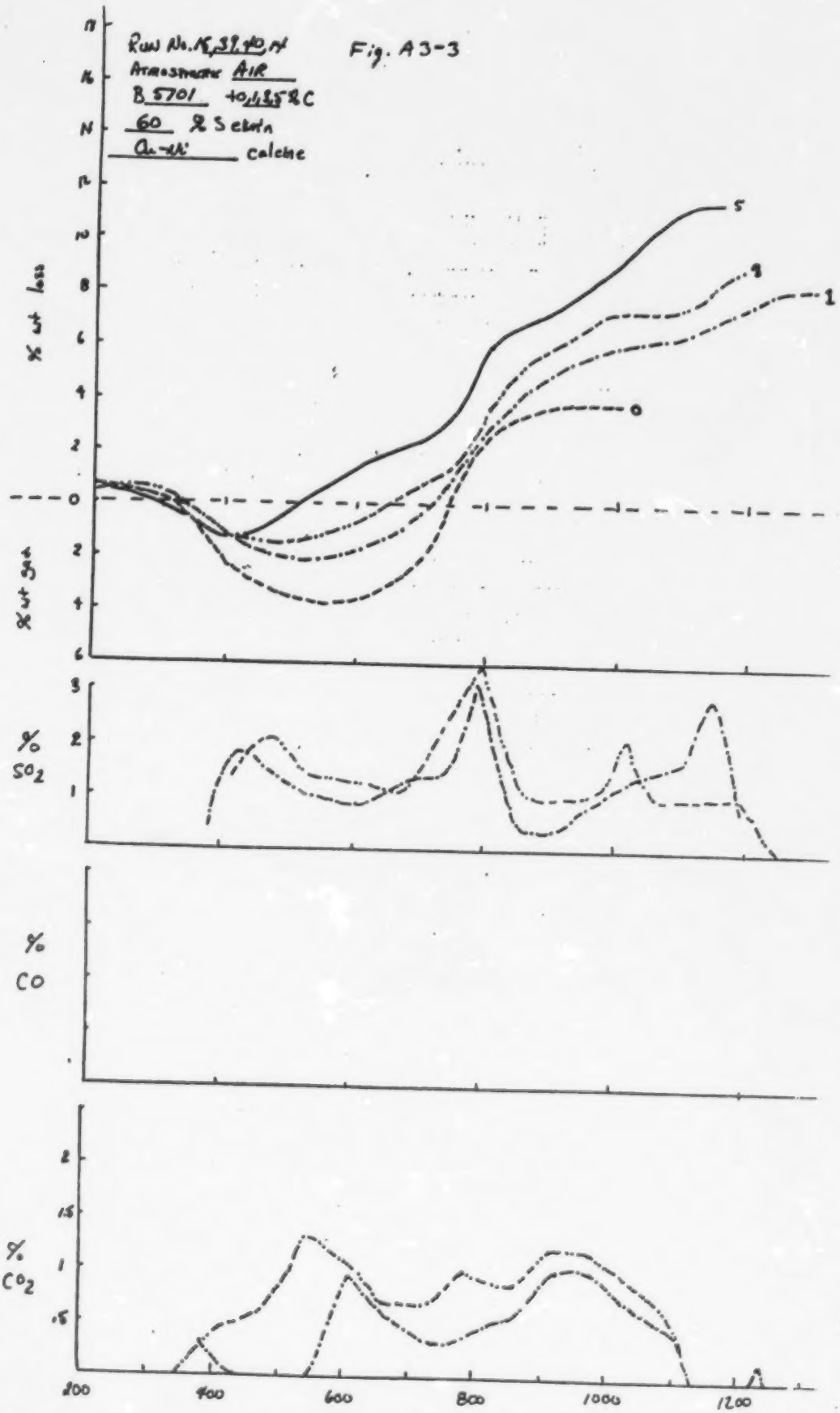
____ % Sebutn

COKE only calcine 0.5 g.



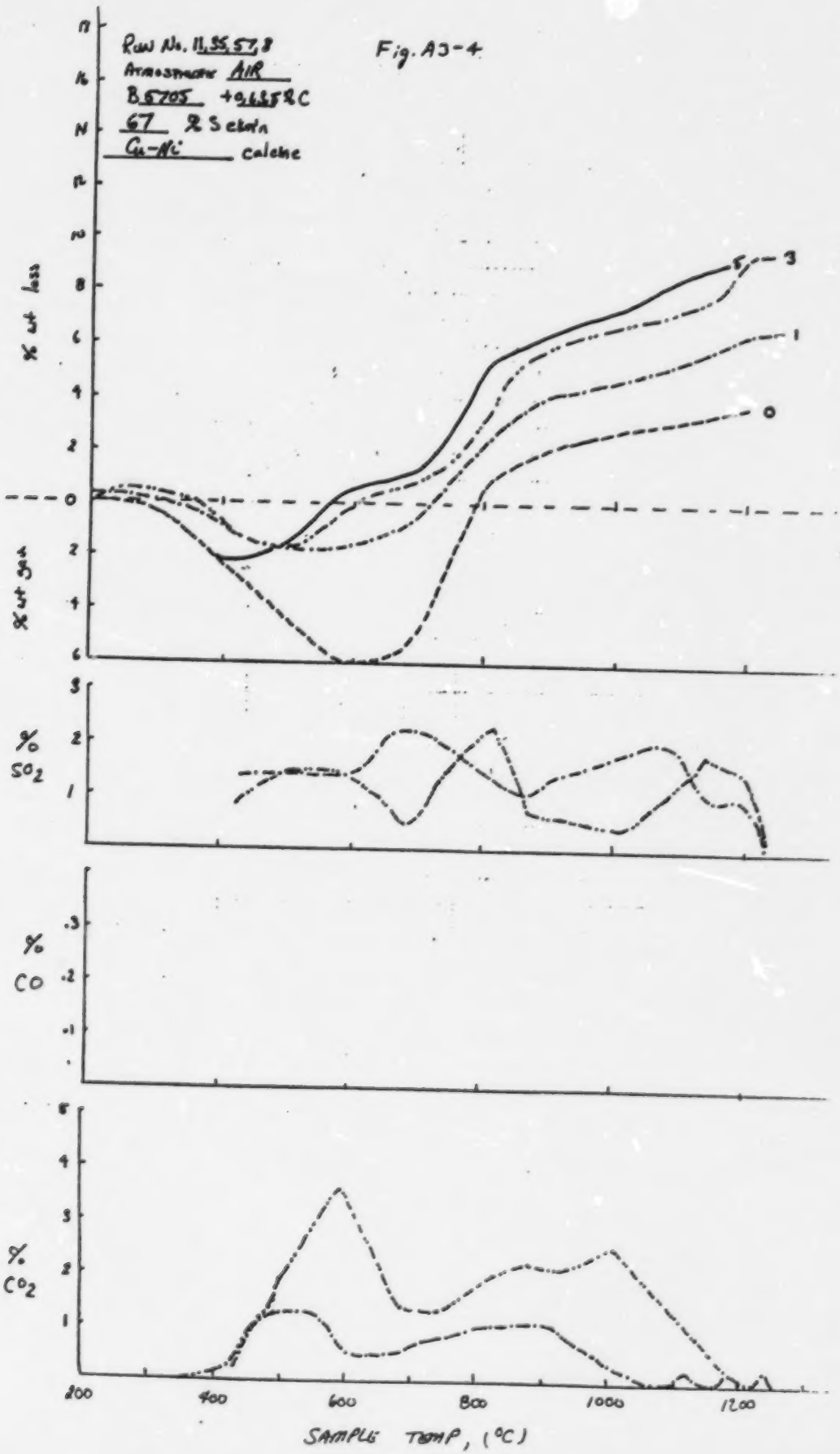

Run No. 47, 51, 55
Atmosphere AIR
B.#/Hr +9435 C
60 % Screen
Cu-Ni calcine
Fig A3-2
% wt loss
% wt gain
% SO2
% CO
% CO2
SAMPLE TEMP, (°C)
200
400
600
800
1000
1200

Run No. K,37,40,41 Fig. A3-3
Atmosphere AIR
B 5701 +0,1,2,5 %C
60 % Sectn
Qu-41 calcine



Run No. 11,55,57,8
Atmosphere AIR
B.S705 +0.665°C
67 % Sulph
Cu-Ni calcine

Fig. A3-4



Run No. 12, 14, 16, 17

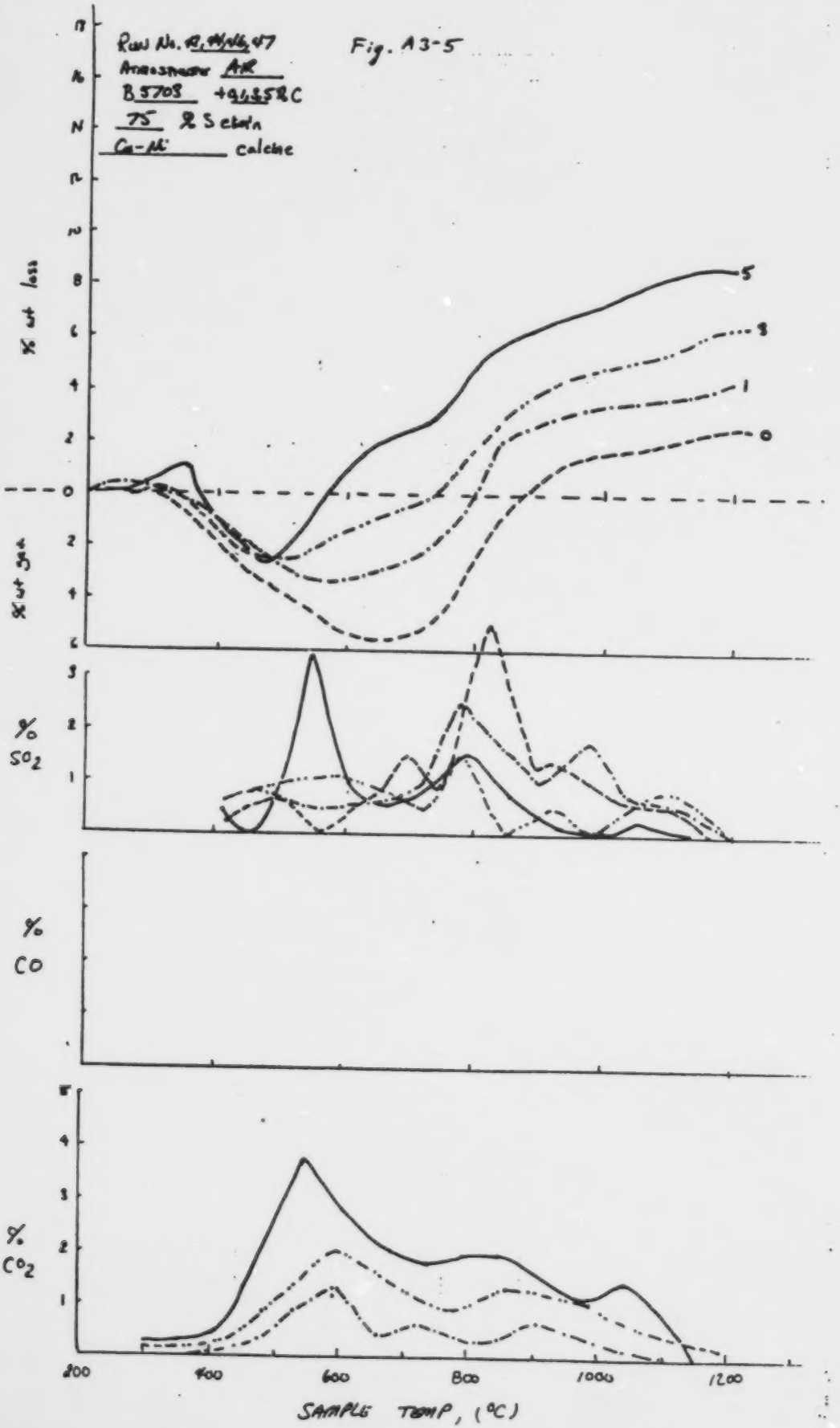
Atmosphere AIR

B.5703 +91.55%C

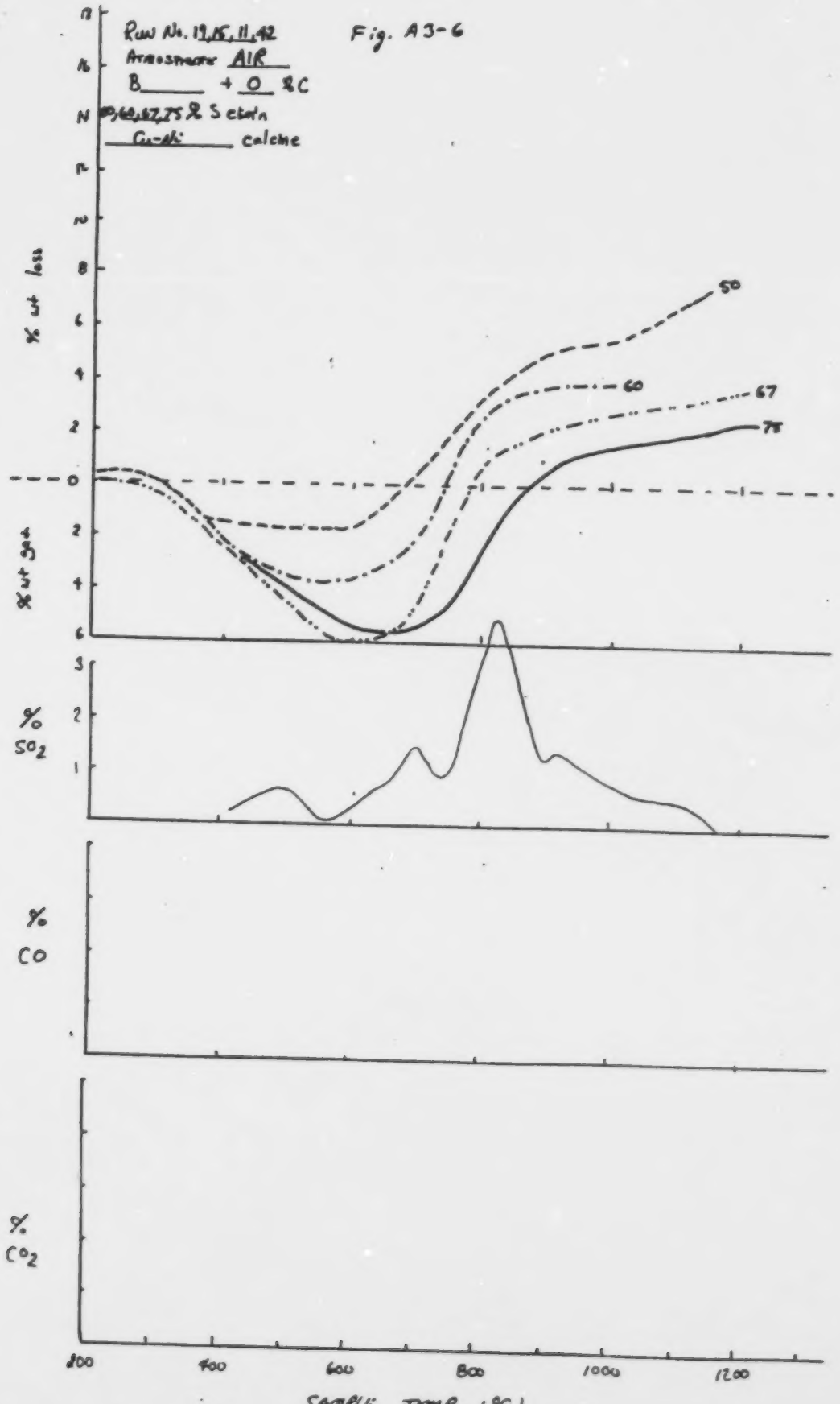
75 % S etc'n

Ca-Al calcine

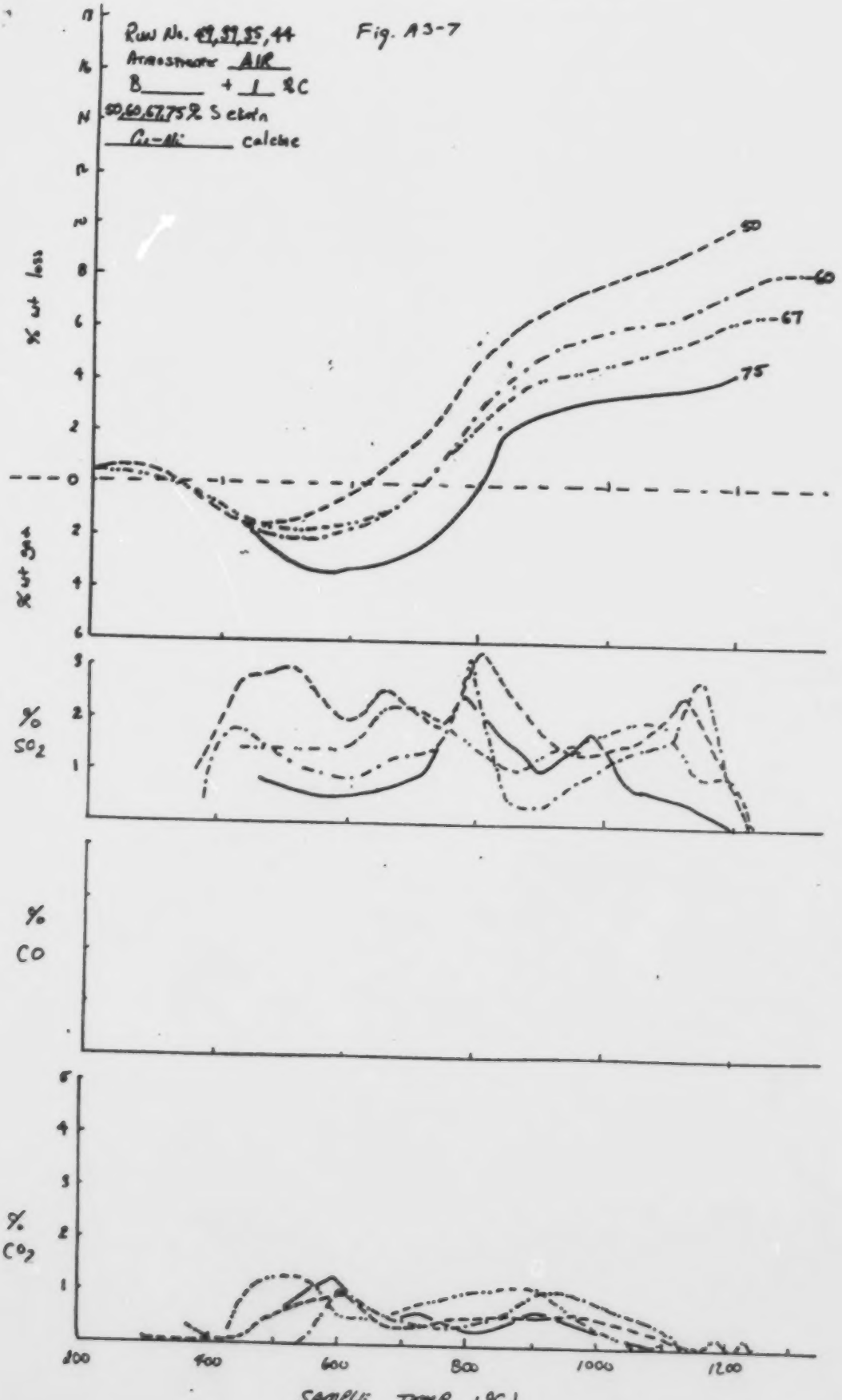
Fig. A3-5

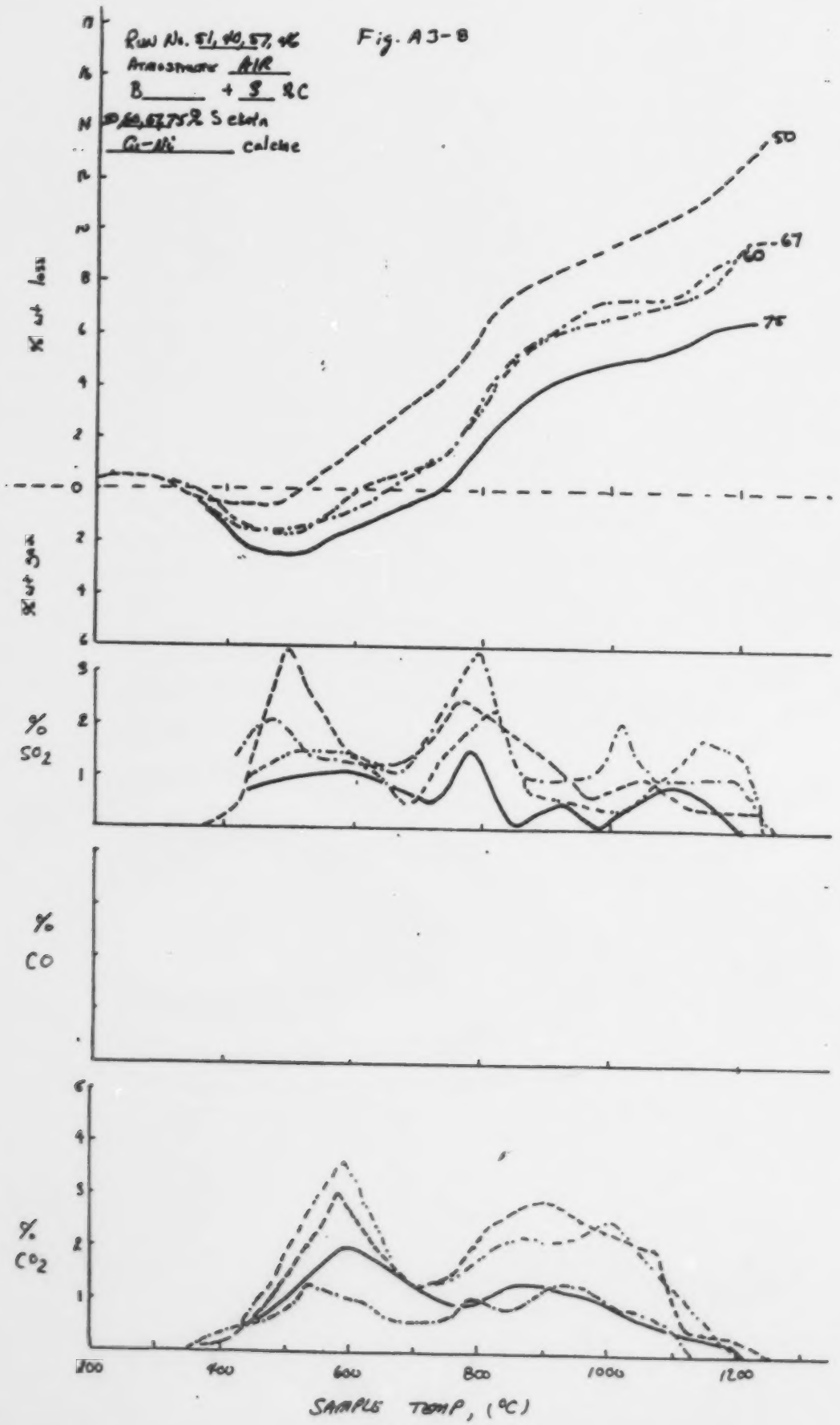


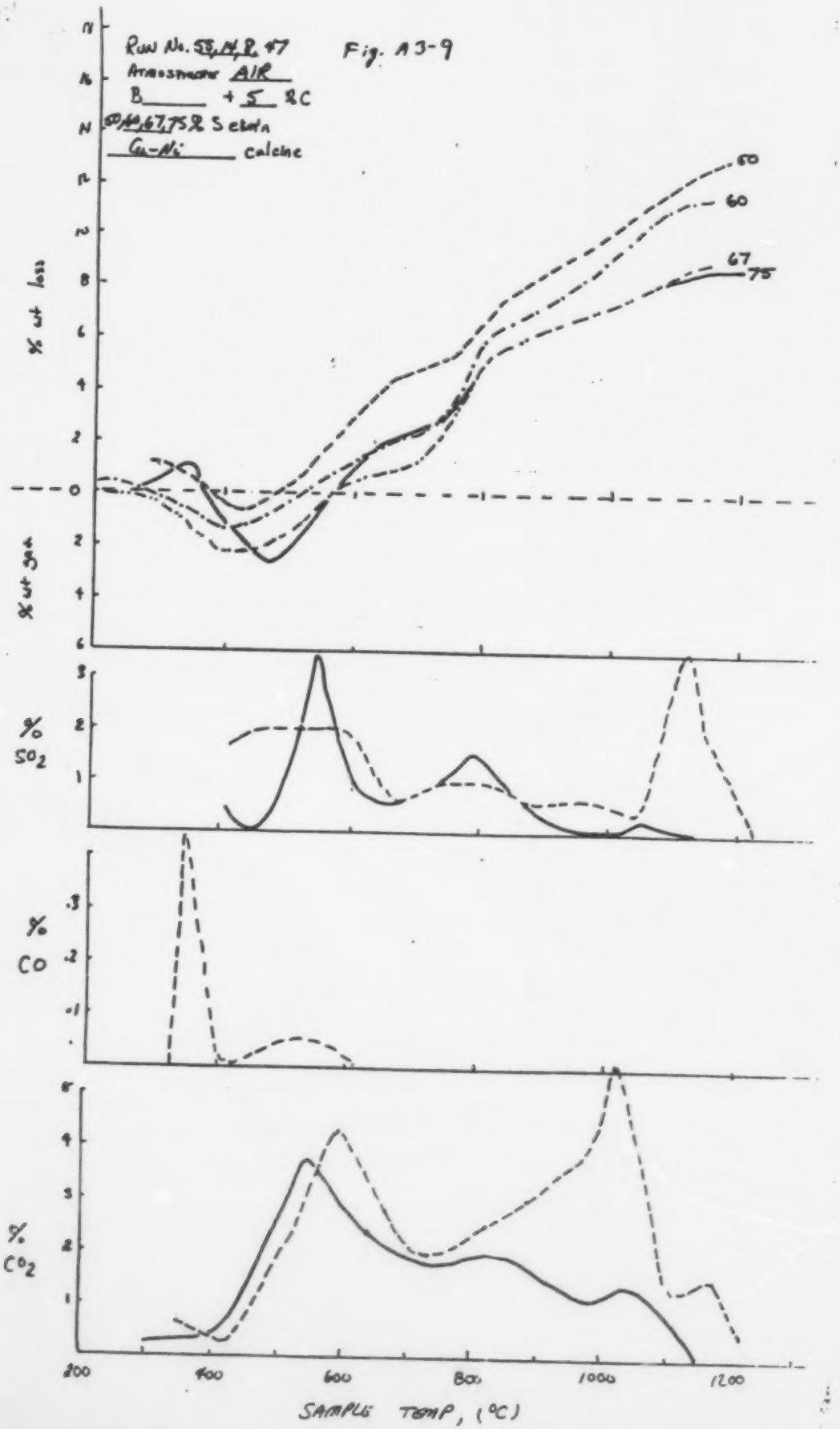
Run No. 19,15,11,42 Fig. A3-6
Atmosphere AIR
B_____ + O 2C
50,60,67,75 & Setoin
Cu-Ni calcine



Run No. 49,57,55,44 Fig. A3-7
Atmosphere AIR
B_____ + 1 %C
50,60,67,75 % S etc'n
Cu-Ni calcine




Run No. 51, 40, 57, 75
Atmosphere AIR
B ____ + 5 %C
40, 57, 75 % Sulfur
Ca-Al ____ calcine
Fig. A3-8
50
60
67
75
% wt loss
% wt gain
% SO2
% CO
% CO2
SAMPLE TEMP, (°C)


Run No. 53, N, P, 67
Atmosphere AIR
B ____ + 5 %C
50, 60, 67, 75 % Selenn
Cu-Ni ____ calcine
Fig. A3-9
% wt loss
% wt gain
50
60
67
75
% SO2
% CO
% CO2
200
400
600
800
1000
1200
SAMPLE TEMP, (°C)